

ETHER-CAPPED POLY(OXYALKYLATED) ALCOHOL SURFACTANTS

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TECHNICAL FIELD

The present invention relates to low-foaming nonionic surfactants and more particularly to ether-capped poly(oxyalkylated) alcohol surfactants which have superior spotting and filming benefits in dishwashing and hard surface cleaning applications.

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BACKGROUND OF THE INVENTION

Due to the varied nature of different cleaning compositions, different surfactants are better suited for some applications while being less suited or totally unsuitable for other applications. Nonionic surfactants, such as alcohol ethoxylates, alkyl polyglycosides, and alkyl glucose amides are of considerable importance in detergent products. For example, under some conditions, nonionic surfactants aid cleaning of greasy soils and inhibit the formation of calcium soap. However, conventional nonionic surfactants designed for effective cleaning in laundry products form liquid crystalline phases on mixing with water. These phases can hinder the rate of mixing with water and lead to undesirable optical properties of thin films on solution drying. For example, conventional nonionics sprayed on the surface of granules to achieve target density can give rise to poor granule dissolution and residue in horizontal axis machine dispensers. Conventional nonionics formulated at high levels in liquid products can lead to poor rates of mixing with water and consumer concern. Conventional nonionics in window and floor cleaners can form visible liquid crystalline films on drying that increase the effort required by the consumer to achieve good results. Similarly, a nonionic surfactant for use in an automatic dishwashing machine would need to minimize foam production and not leave undesirable spots and films on the cleaned surfaces.

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On account of the foregoing technical constraints as well as consumer needs and demands, product compositions are undergoing continual change and improvement.

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Moreover environmental factors such as the need for biodegradable materials, the restriction of phosphate, the desirability of providing ever-better cleaning results with less product, providing less thermal energy demand, and less water to assist the washing process, have all driven the need for improved compositions.

5 Accordingly, the need remains for new surfactants which are suitable for use in a variety of compositions which can provide improve dissolution of solid products (like bars and tablets) and granular products, improved rates of mixing with water as with liquid products, improved streaking and filming performance as in hard surface cleaners and automatic dishwashing, good cleaning, suds control and good biodegradability while
10 avoiding incompatibility with other cleaning surfactants and/or bleach.

BACKGROUND ART

U.S. Patent 4,272,394, WO 94/22800, WO 93/04153, WO96/00253 and WO 98/17379.

SUMMARY OF THE INVENTION

15 This need is met by the present invention wherein a low-foaming nonionic surfactant is provided. The low-foaming nonionic surfactant, either alone or in combination with other surfactants, provides improved spotting and filming performance as well as improved cleaning performance on greasy soils and suds or foam suppression in certain applications. While not wishing to be bound by theory, it is believed the
20 surfactants of the present invention deliver superior spotting and filming benefits via improved sheeting action. As for improved cleaning performance on greasy soils, such benefits are shown when the alcohol surfactants of the present invention are optionally employed in conjunction with a high cloud point nonionic surfactant, an amphoteric surfactant or a hydrophobic anionic surfactant, as disclosed in detail herein. Lastly,
25 certain alcohol surfactants of the present invention may also act to reduce the suds or foaming associated with food soils or various other cleaning agents.

In accordance with an aspect of the present invention, an ether-capped poly(oxyalkylated) alcohol surfactant is provided. The alcohol has the formula:



wherein, R is selected from the group consisting of linear or branched, saturated or unsaturated, substituted or unsubstituted, aliphatic or aromatic hydrocarbon radicals having from about 1 to about 30 carbon atoms; R¹ may be the same or different, and is independently selected from the group consisting of branched or linear C₂ to C₇ alkylene in any given molecule; x is a number from 1 to about 30; and R² is selected from the group consisting of:

- (i) a 4 to 8 membered substituted, or unsubstituted heterocyclic ring containing from 1 to 3 hetero atoms; and
- (ii) linear or branched, saturated or unsaturated, substituted or unsubstituted, cyclic or acyclic, aliphatic or aromatic hydrocarbon radicals having from about 1 to about 30 carbon atoms;

provided that when R² is (ii) then either at least one of R¹ is other than C₂ to C₃ alkylene or R² has from 6 to 30 carbon atoms.

These and other aspects, features and advantages will become apparent to those of ordinary skill in the art from a reading of the following detailed description and the appended claims. All percentages, ratios and proportions herein are by weight, unless otherwise specified. All temperatures are in degrees Celsius (°C) unless otherwise specified. All documents cited are in relevant part, incorporated herein by reference.

DETAILED DESCRIPTION OF THE INVENTION

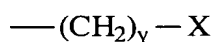
Once again, the present invention is directed toward a low-foaming nonionic surfactant for use in detergent compositions. The surfactant of the present invention is of the formula:



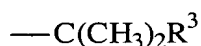
In one aspect of the present invention R is a linear or branched, saturated or unsaturated, substituted or unsubstituted, aliphatic hydrocarbon radical having from about 1 to about 20 carbon atoms, even more preferably R is a linear or branched, saturated, aliphatic hydrocarbon radicals having from about 4 to about 18 carbon atoms.

In one aspect of the present invention R, R¹ and R² are selected such that the ether-capped poly(oxyalkylated) alcohol surfactant contains one or more chiral carbon atoms.

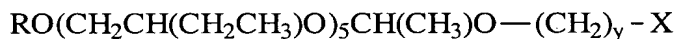
In the novel compounds of the present invention, when R^2 is (ii) then either at least one of R^1 is other than C_2 to C_3 alkylene or R^2 has from 6 to 30 carbon atoms. That is, when R^2 is (ii) R^2 is either linear or branched, saturated or unsaturated, substituted or unsubstituted, aliphatic or aromatic hydrocarbon radicals having from about 6 to about 30 carbon atoms or linear or branched, saturated or unsaturated, substituted or unsubstituted, aliphatic or aromatic hydrocarbon radicals having from about 1 to about 30 carbon atoms, with at least one of R^1 is other than C_2 to C_3 alkylene. For example, when R^2 is a hydrocarbon of the formula:



where, y and X are described hereafter, or R^2 is a hydrocarbon radical of the formula:



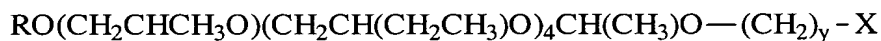
where, R^3 is described hereafter, then at least one of R^1 is other than C_2 to C_3 alkylene. For example, if x is 5, and R^2 was $(CH_2)_y-X$, then the ether-capped poly(oxyalkylated) alcohol could have the formula:



or



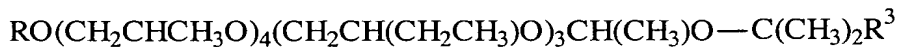
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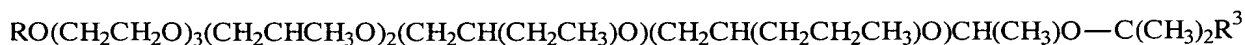
Similarly, for example if R^2 was $-C(CH_3)_2R^3$ and x was 7, then the ether-capped poly(oxyalkylated) alcohol could have the formula:



or

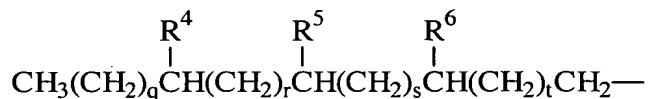


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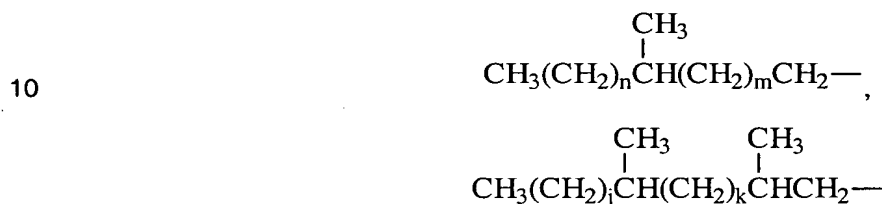


These above examples are included merely for illustrative purposes and are not to be construed in any manner as limiting of the scope of the present invention.

In one aspect of the present invention, R is a hydrocarbon radical of the formula:

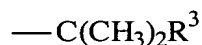


- 5 wherein R⁴, R⁵, and R⁶ are each independently selected from hydrogen, and C₁-C₃ alkyl, more preferably hydrogen, C₁-C₂ alkyl, even more preferably hydrogen, and methyl, provided that R⁴, R⁵, and R⁶ are not all hydrogen and, when t is 0, at least R⁴ or R⁵ is not hydrogen; q, r, s, t are each independently integers from 0 to 13. In one embodiment of this aspect of the present invention R is selected from the formulas:



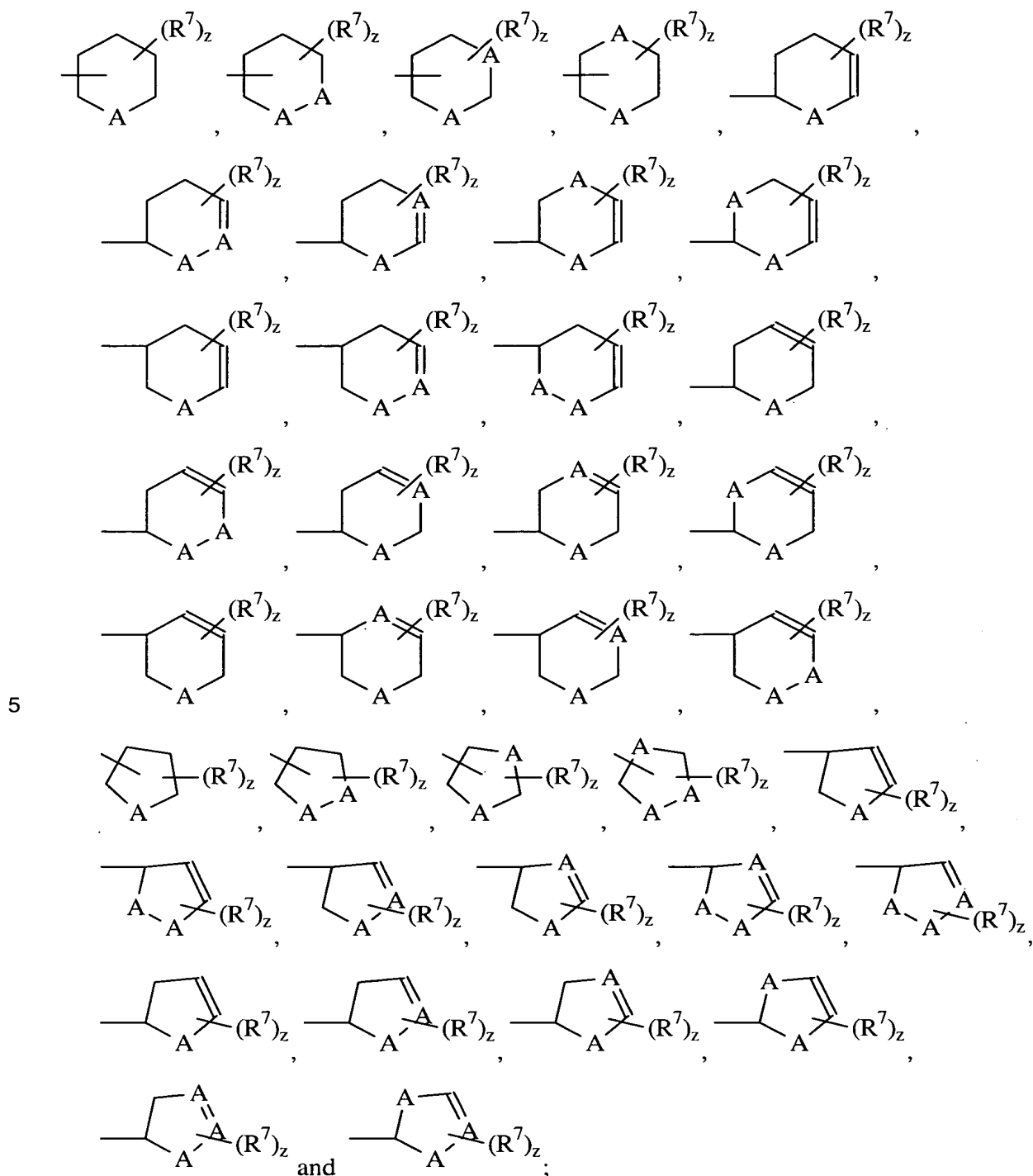
wherein n, m, j and k are each independently integers from 0 to 13.

In one aspect of the present invention R² is a hydrocarbon radical of the formula:



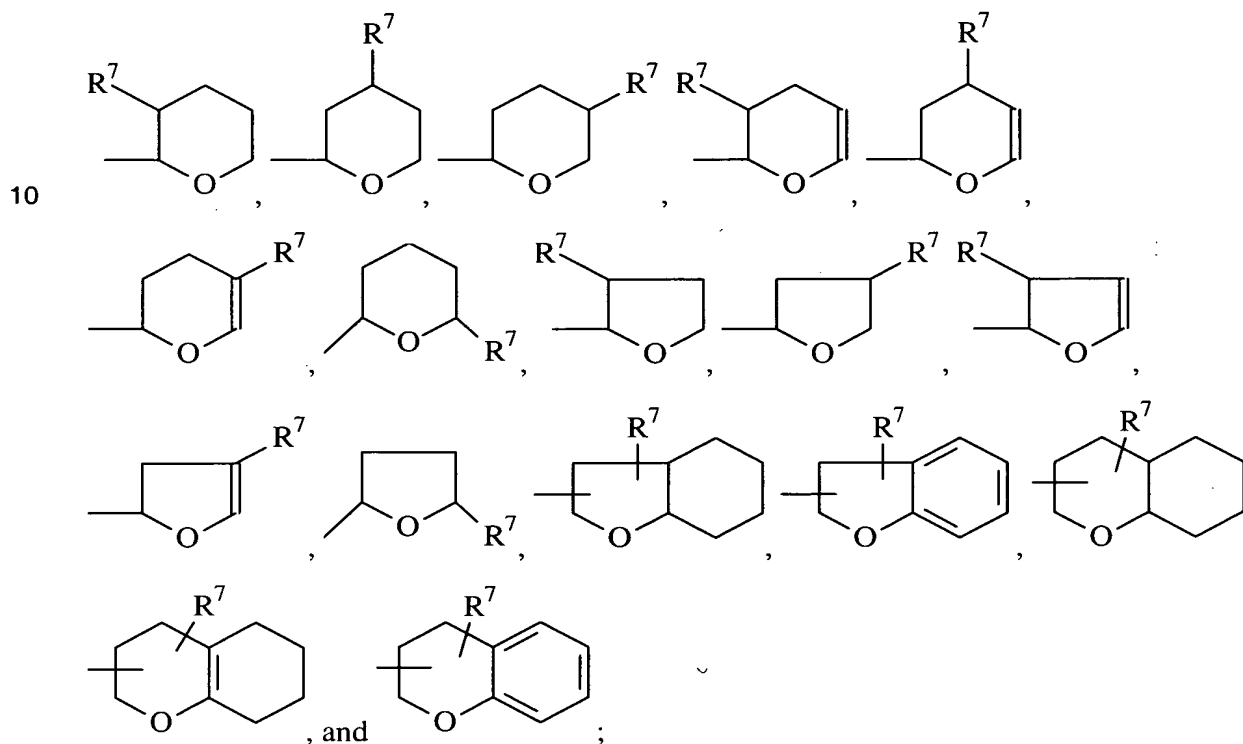
- 15 R³ is selected from the group consisting of linear or branched, saturated or unsaturated, substituted or unsubstituted, aliphatic or aromatic hydrocarbon radicals having from about 1 to about 30, more preferably 1 to 20, even more preferably 1 to 15, carbon atoms, provided that when R³ is methyl, R is branched. In one embodiment of this aspect of the present invention, R³ is ethyl.

- 20 In one aspect of the present invention R² is a 4 to 8 membered substituted, or unsubstituted heterocyclic ring containing from 1 to 3 hetero atoms. In one embodiment of this aspect of the invention the hetero atoms are selected from the group comprising oxygen, nitrogen, sulfur and mixtures thereof. In one embodiment of this aspect of the invention R² is a 5 or 6 member heterocycle. In another embodiment of this aspect of the present invention R² is selected from the group consisting of:
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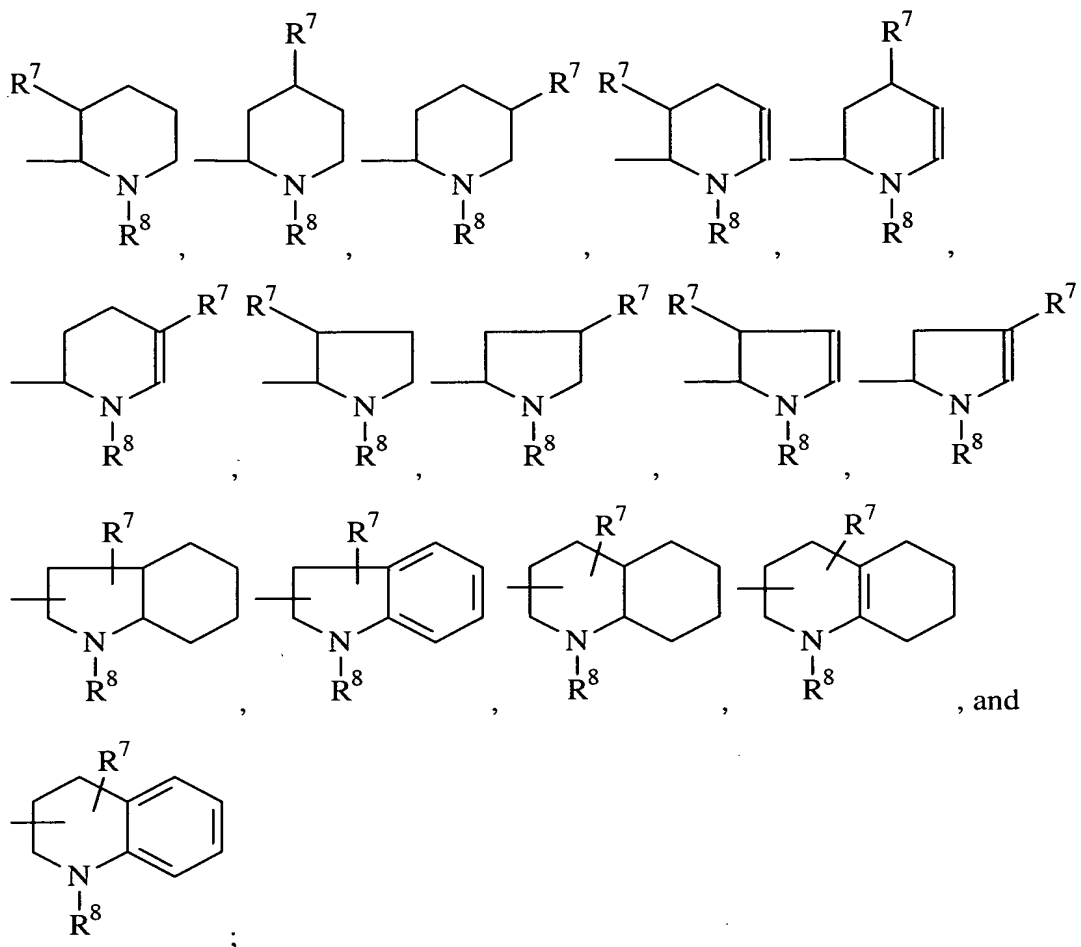
- unsaturated, substituted or unsubstituted, alicyclic or aromatic hydrocarbon or alkoxy radical having, from about 1 to about 10 carbon atoms, which is fused to the heterocyclic ring; each A is independently selected from the group consisting of O, and $N(R^8)_a$, wherein R^8 is independently selected from the group consisting of hydrogen, linear or branched, saturated or unsaturated, substituted or unsubstituted, aliphatic hydrocarbon radical having from about 1 to about 10 carbon atoms, and a is either 0 or 1; z is an integer from 1 to 3.
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In another embodiment of this aspect of the present invention R^2 is selected from the group consisting of:



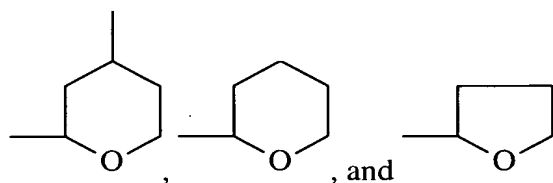
wherein R^7 is defined as above.

- 15 In another embodiment of this aspect of the present invention R^2 is selected from the group consisting of:

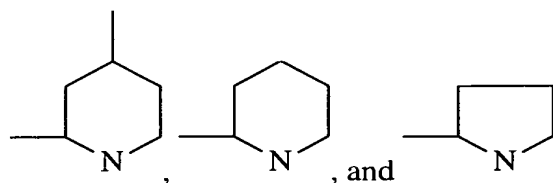


5 wherein R^7 and R^8 are defined as above.

In another embodiment of this aspect of the present invention R^2 is selected from the group consisting of:

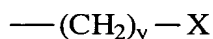


10 In another embodiment of this aspect of the present invention R^2 is selected from the group consisting of:



In one aspect of the present invention R^2 is a 7 to 13 membered substituted, or unsubstituted polycyclic ring. In one embodiment of this aspect of the present invention R^2 is selected from the group consisting of substituted, or unsubstituted adamantane, substituted, or unsubstituted norbornane, substituted, or unsubstituted nortricyclene, and substituted, or unsubstituted bicyclo[2.2.2]octane. In another embodiment of this aspect of the present invention R^2 is a substituted, or unsubstituted adamantane.

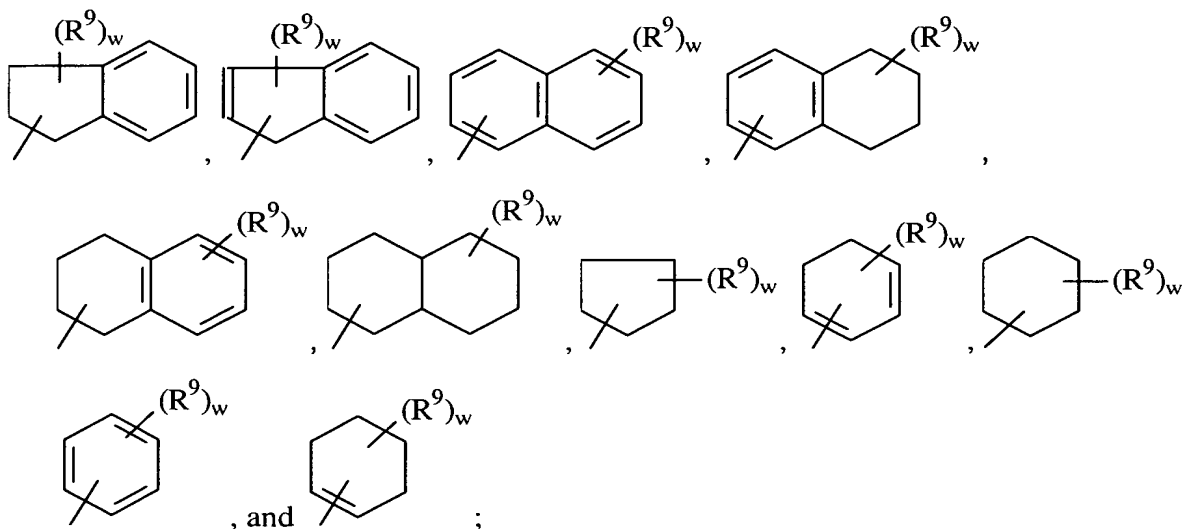
In one aspect of the present invention R^2 is a hydrocarbon of the formula:



wherein, y is an integer from 0 to 7, X , is a 4 to 8 membered substituted, or unsubstituted, saturated or unsaturated cyclic or aromatic hydrocarbon radical. In another embodiment of this aspect of the present invention y is an integer from 1 to 2, and X is selected from the group consisting of 5 to 8 membered substituted, or unsubstituted, aromatic hydrocarbon radical.

In another embodiment of this aspect of the present invention y is 0 and X , is a 5 or 6 membered substituted, or unsubstituted, saturated or unsaturated cyclic or aromatic hydrocarbon radical.

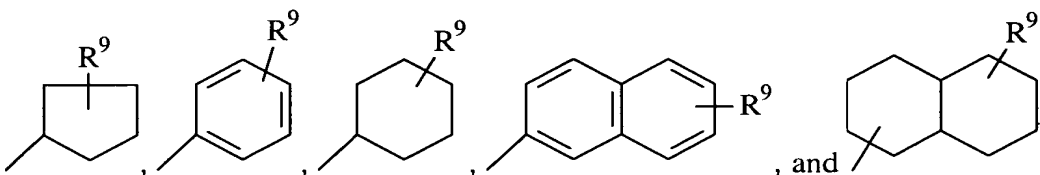
In another embodiment of this aspect of the present invention X is selected from the group consisting of:



wherein each R^9 is independently selected from the group consisting of hydrogen, linear or branched, saturated or unsaturated, substituted or unsubstituted, aliphatic hydrocarbon

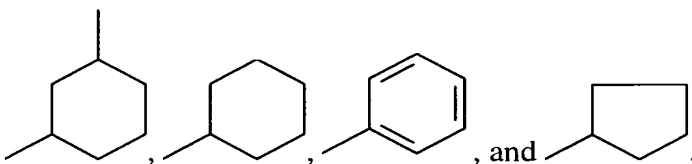
or alkoxy radical having from about 1 to about 10 carbon atoms, or R^9 is a saturated or unsaturated, substituted or unsubstituted, alicyclic or aromatic hydrocarbon radical having, from about 1 to about 10 carbon atoms, which is fused to the ring; w is an integer from 1 to 3.

- 5 In another embodiment of this aspect of the present invention X is selected from the group consisting of:



wherein R^9 is defined as above.

- 10 In another embodiment of this aspect of the present invention X is selected from the group consisting of:



- 15 In one aspect of the present invention R^2 is a linear or branched, saturated or unsaturated, substituted or unsubstituted, aliphatic or aromatic hydrocarbon radicals having from about 1 to about 30 carbon atoms, more preferably R^2 is a linear or branched, saturated or unsaturated, substituted or unsubstituted, aliphatic hydrocarbon radical having from about 1 to about 20 carbon atoms, even more preferably R^2 is a linear or branched, saturated, aliphatic hydrocarbon radicals having from about 4 to about 18 carbon atoms.

- 20 In one aspect of the present invention, when x is greater than 2, R^1 may be the same or different. That is, R^1 may vary between any of the alkyleneoxy units as described above. For instance, if x is 3, R^1 may be selected to form ethyleneoxy(EO) or propyleneoxy(PO) and may vary in order of (EO)(PO)(EO), (EO)(EO)(PO); (EO)(EO)(EO); (PO)(EO)(PO); (PO)(PO)(EO) and (PO)(PO)(PO). Of course, the integer three is chosen for example only and the variation may be much larger with a higher
25 integer value for x and include, for example, multiple (EO) units and a much small

number of (PO) units. Similarly, ethylene, and propylene are chosen for example only and the variation may be much larger with selection of linear or branched butylene, pentylene, hexylene and/or heptylene.

The surfactants of the present invention can be prepared via a variety of different process. In one aspect of the present invention, the surfactants may be prepared by reacting a vinyl ether of the formula:



wherein R^2 is as defined above; with an alkoxyated alcohol of the formula



wherein R , R^1 , and x , are as defined above, in the presence of a catalyst to form the ether-capped poly(oxyalkylated) alcohol.

In one embodiment of this aspect of the present invention the step of reacting of vinyl ether with alkoxyated alcohol is conducted in the presence of a catalyst. Suitable catalysts include Lewis acids; acids and their salts, both organic and inorganic; pyridinium salts; polymers; clays, such as, Spanish sepiolite clay, GIRDLER K-10; aluminosilicates or zeolites, such as HZS-360 zeolite, H-Y zeolite; activated carbon, such as sulfonated charcoal; transition metal complexes, such as, molybdenyl(VI) acetylacetonate; transition metal salts, such as lanthanum trichloride, ceric ammonium nitrate; 2,3-dichloro-5,6-dicyano-p-benzoquinone; bis(trimethylsilyl)sulfate, and mixtures thereof.

Suitable Lewis acids include, but are not limited to, $TiCl_4$, $Ti(O^iPr)_4$, $ZnCl_2$, $SnCl_2$, $AlCl_3$, platinum dichloride, copper(II) chloride, phosphorous pentachloride, phosphorous trichloride, cobalt(II) chloride, zinc oxide, iron(II) chloride and $BF_3 \cdot OEt_2$.

Suitable inorganic acids include, mineral acids, such as, phosphoric acid, sulfuric acid, hydrochloric acid, phosphorous oxychloride, aluminium phosphate and ammonium chloride. Furthermore, the mineral acids or their salts can optionally be adsorbed on to a substrate, such as, silica gel, or alumina. For example sulfuric acid adsorbed on silica gel, or alumina impregnated with zinc chloride.

Suitable organic acids include: carboxylic acids, such as, acetic acid, oxalic acid, glycolic acid, citric acid, tartaric acid, maleic acid and oxydisuccinic acid; halogenated carboxylic acids, such as, trifluoroacetic acid, heptafluorobutyric acid, dichloroacetic acid,

and trichloroacetic acid; and sulfonic and sulfinic acids and their salts such as, p-toluenesulfonic acid, p-toluenesulfinic acid, methanesulfonic acid, trifluoromethanesulfonic acid, 4-bromobenzene sulfonic acid, naphthalene sulfonic acid, (\pm)-10-camphor sulfonates, and alkyl benzene sulfonic acid.

5 Suitable pyridinium salts, include, but are not limited to, pyridinium p-toluenesulfonate (PPTS), pyridinium p-toluenesulfinate, pyridinium hydrochloride, pyridinium hydrobromide, pyridinium hydrogen bisulfate, pyridinium hydrogen sulfate and mixtures thereof.

10 Suitable transition metal, include, but are not limited to, molybdenyl(VI) acetylacetonate; transition metal salts, such as lanthum trichloride, ceric ammonium nitrate; 2,3-dichloro-5,6-dicyano-p-benzoquinone, mercury(II) acetate, mercury(II) trifluoroacetate, copper(II) acetylacetonate and tetracarbonylbis(cyclopentadienyl)diiron.

15 Suitable polymers, include, but are not limited to, polymeric ion exchange resins, or polyvinyl pyridines. Suitable polymeric ion exchange resins include those of the Amberlyst series, such as AMBERYLST®15, available from Rohm & Haas, the DOWEX® series, such as, DOWEX 50X8-50 available from Dow; REILLEX 424, available from Reilly Industries; the Amberlite series, such as AMBERLITE IRA-400, or AMBERLITE IR-118, available from Rohm & Haas; available from United Catalyst ; the ENVIROCAT series, such as ENVIROCAT EPZG, available from Contract Chemicals; 20 and combinations thereof. Suitable polyvinyl pyridines can be unsubstituted or substituted, such as substituted on the vinyl group and/or on the pyridine ring. Examples of suitable polyvinyl pyridines include, but are not limited to, poly(4-vinylpyridine trifluoromethanesulfonate), poly(2-vinylpyridine trifluoromethanesulfonate), poly(4-vinylpyridine p-toluenesulfonate), poly(2-vinylpyridine p-toluenesulfonate), poly(4-vinylpyridine chloride), poly(2-vinylpyridine chloride), poly(4-vinylpyridine bromide), 25 poly(2-vinylpyridine bromide), and mixtures thereof. These polymeric catalysts have the additional advantage of being easy to separate from the surfactant produced.

30 Other suitable catalysts include, bis(trimethylsilyl)sulfate, iodotrimethylsilane, allyltrimethyl silane, hexamethyldisilane, iodine, bromine, iron(II) sulfate, triphenylphosphine, aluminium sulfate, alkylether sulfuric acids, alkyl sulfuric acids,

lithium perchlorate, lithium tetrafluoroborate, acetonitriltriphenylphosphonium bromide, zirconium hydroxide, potassium cyanide, and platinum oxide.

Preferred catalysts include the sulfonic acids, Lewis acids, polyvinyl pyridines, methanesulfonic acid, AMBERYLST®15, acidic versions of DOWEX® and pyridinium
5 p-toluenesulfonate (PPTS) with polyvinyl pyridines, pyridinium p-toluenesulfonate (PPTS), p-toluenesulfonic acid, DOWEX®, AMBERYLST®15 and methanesulfonic acid, being the most preferred.

Mixtures of catalysts are also within the scope of the present invention. Similarly, the uses of supported, such as in a column for a continuous reaction, and unsupported
10 catalysts are also within the scope of the present invention.

The catalysts are preferably employed at amounts of about 0.1 mol % to about 20.0 mol %, more preferably from about 0.1 mol % to about 10.0 mol %, even more preferably from about 0.1 mol % to about 5.0 mol %, even more preferably still from about 0.1 mol % to about 2.0 mol %, even more preferably still from about 0.2 mol % to
15 about 1.0 mol %. Other suitable catalysts can be found in US patent No. U.S. Patent 4,272,394, and in PCT publications, WO 94/22800, WO 93/04153, WO96/00253 and WO 98/17379 all of which are incorporated herein by reference.

In one embodiment of this aspect of the present invention the reaction is conducted in the presence of a solvent, or mixtures of solvents. It is preferred that the
20 solvent be a polar aprotic solvent. Suitable solvents include, but are not limited to, hexane, benzene, toluene, xylene, mesitylene, dichloromethane, tetrahydrofuran, dioxane, chloroform, diethylether, methyl tert-butylether, acetone, acrylonitrile, or the like. Furthermore, the reaction is preferably conducted at temperatures ranging from about -20°C to about 300°C, and more preferably from about -10°C to about 250°C. Lastly, the
25 reaction is preferably conducted at pressures ranging from about 0.5 atmospheres to about 100 atmospheres, and more preferably from about 0.8 atmospheres to about 10 atmospheres.

In another embodiment of this aspect of the present invention the step of reacting vinyl ether with alkoxylated alcohol is conducted in the absence of a solvent.

Further disclosure on suitable solvents and catalysts can be found in "Advanced Organic Chemistry", by Jerry March, 4th ed., Wiley-Interscience, 1992, "Comprehensive Organic Transformations" by Richard C. Larock, VCH Publishers, 1989, and "Protective Groups in Organic Synthesis" 3RD ed. by Theodora W. Greene and Peter G. M. Wuts, 5 Wiley-Interscience, 1999 the relevant portions of which are incorporated herein by reference.

In one embodiment of the present invention, the process is performed as a batch process. That is, the reaction is let proceeded to completion, or near completion, and then final product is removed. In another embodiment of the present invention, the process is 10 performed as a continuous process. That is, the product of the process is continuously removed from the reaction vessel while staring material is added at a comparable rate.

In one embodiment of the present invention the vinyl ether is reacted with the alkoxylated alcohol at a mole ratio of from about 5 to about 1, more preferably from about 3 to about 1, more preferably still from about 1.5:1 to about 0.90:1 mole %.

15 In one embodiment of the process of the present invention the process may be conducted in an inert gas. This may be done by sparging with any suitable inert gas, such as nitrogen, helium, neon, or argon.

In one embodiment of the present invention reaction step (c) may be followed by optional step (d). Step (d), is a step in which the reaction step (c) is quenched, preferably 20 by the addition of base. The amount of the ether capped poly(oxyalkylated) alcohol surfactant present in the reaction mixture will depend upon many factors, including but not limited to, starting materials, temperature, catalyst selection and the like. Quenching stops the reaction, of the starting materials, and ensures that any ether capped poly(oxyalkylated) alcohol surfactant produced does not undergo further reaction or revert 25 back to the starting materials. The quenching of step (c) produces a mixture which contains ether capped poly(oxyalkylated) alcohol surfactant, as well as, unreacted starting materials, catalyst and the products of any side reactions. In one embodiment of this present invention the quenching of the reaction of step (c) is done when the reaction mixture preferably contains at least 90%, more preferably 95% by weight of ether capped 30 poly(oxyalkylated) alcohol surfactant. The remaining 10%, more preferably 5% by

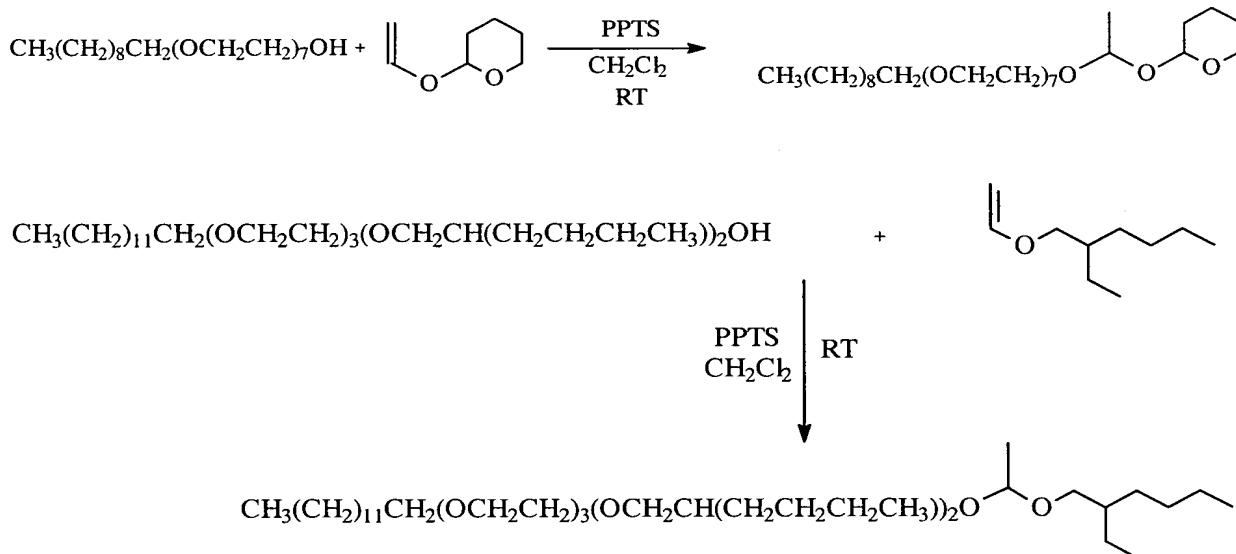
weight, comprises, unreacted starting material as well as products of side reactions, such as byproduct acetals. In one aspect of this embodiment of the present invention the base may be optionally selected from the group consisting of alkali metal carbonates, alkali metal bicarbonates alkali metal hydroxides, alkali metal alcoholates, alkanolamines, alkylamines, aromatic amines and mixtures thereof. In a further aspect of the present invention the base may be optionally selected from the group consisting of potassium carbonate, sodium carbonate, sodium bicarbonate sodium methoxylate, sodium ethoxylate, potassium tert-butyloxyate, triethylamine, triethanolamine and mixtures thereof. In another aspect of this embodiment of the present invention the base may be in the form of an aqueous solution. In a further aspect of this embodiment of the present invention the aqueous solution may be at a temperature of from about 20°C to about 60°C.

The expression "product of step (c)" is meant to include not only the ether-capped poly(oxyalkylated) alcohol surfactant but also any unreacted starting materials or any materials produced from side reactions, such as dimers, which would be present at the conclusion of step (c).

In one embodiment of the present invention the process of the present invention may optionally further comprise a step (e). Step (e) is removal of color bodies and/or odors from the product of steps (c) or (d). In one aspect of this embodiment of the present invention removal of the color bodies and/or odors is obtained by contacting the product of steps (c) or (d) with a reagent. The reagent can either be an oxidant, or a reductant. Suitable oxidants include hydrogen peroxide. Suitable reductants include sodium borohydride, and hydrogen over a palladium/carbon catalyst. In a further aspect of this embodiment of the present invention the color bodies and/or odors are removed by contacting the product of steps (c) or (d) first with an oxidant and then a reductant or first with a reductant and then an oxidant.

In one embodiment of the present invention the ether-capped poly(oxyalkylated) alcohol surfactant produced in steps (c) may optionally removed from the product of steps (c) or (d) by centrifuging.

Some representative examples of this synthetic route of this aspect of the invention is demonstrated via the following diagrams.



The ether-capped poly(oxyalkylated) alcohol surfactant product is then collect by means common in the art such as extraction. If desired, the surfactant may be further treated by stripping, distillation or various other means before use. The surfactants made by the process disclosed herein may contain related impurities which will not adversely affect performance.

Cleaning Adjunct Materials and Methods:

In general, cleaning adjunct is any material required to transform a composition containing only the minimum essential ingredients into a composition useful for cleaning purposes, such as fabric cleaning, tableware cleaning, hard surface cleaning, or personal cleansing (such as a body wash or a shampoo). Additionally, the surfactants of the present invention are also useful in post-wash cycle compositions, such as in fabric softeners and anti-static compositions. In preferred embodiments, cleaning adjuncts are easily recognizable to those of skill in the art as being absolutely characteristic of cleaning products, especially of cleaning products intended for direct use by a consumer in a domestic environment.

The precise nature of these additional components, and levels of incorporation thereof, will depend on the physical form of the composition and the nature of the cleaning operation for which it is to be used.

Preferably, the adjunct ingredients if used with bleach should have good stability therewith. Certain preferred detergent compositions herein should be boron-free and/or phosphate-free as required by legislation. Levels of adjuncts are from about 0.00001% to about 99.9%, by weight of the compositions. Use levels of the overall compositions can vary widely depending on the intended application, ranging for example from a few ppm in solution to so-called "direct application" of the neat cleaning composition to the surface to be cleaned.

Common adjuncts include builders, co-surfactants, enzymes, polymers, bleaches, bleach activators, catalytic materials and the like excluding any materials already defined hereinabove as part of the essential component of the inventive compositions. Other adjuncts herein can include diverse active ingredients or specialized materials, for example, dispersant polymers (e.g., from BASF Corp. or Rohm & Haas), color speckles, silvercare, anti-tarnish and/or anti-corrosion agents, dyes, fillers, germicides, bactericides, alkalinity sources, hydrotropes, anti-oxidants, enzyme stabilizing agents, suds boosters, buffers, anti-fungal agents, mildew control agents, insect repellents, anti-corrosive aids, chelants suds suppressors thickeners, abrasives, pro-perfumes, perfumes, solubilizing agents, carriers, processing aids, pigments, and, for liquid formulations, solvents, as described in detail hereinafter.

Co-surfactants:

The surfactant system of the compositions according to the present invention may further comprise additional surfactants, herein also referred to as co-surfactants, preferably selected from: anionic surfactants, preferably selected from the group of alkyl alkoxylated sulfates, alkyl sulfates, alkyl disulfates, and/or linear alkyl benzenesulfonate surfactants; cationic surfactants, preferably selected from quaternary ammonium surfactants; nonionic surfactants, preferably alkyl ethoxylates, alkyl polyglucosides, polyhydroxy fatty acid amides, and/or amine or amine oxide surfactants; amphoteric surfactants, preferably selected from betaines and/or polycarboxylates (for example polyglycinates); and zwitterionic surfactants.

A wide range of these co-surfactants can be used in the cleaning compositions of the present invention. A typical listing of anionic, nonionic, ampholytic and zwitterionic

classes, and species of these co-surfactants, is given in US Patent 3,664,961 issued to Norris on May 23, 1972. Amphoteric surfactants are also described in detail in "Amphoteric Surfactants, Second Edition", E.G. Lomax, Editor (published 1996, by Marcel Dekker, Inc.). Suitable surfactants can be found in U.S. Patent applications Serial

5 Nos. 60/032,035 (Docket No. 6401P), 60/031,845 (Docket No. 6402P), 60/031,916 (Docket No. 6403P), 60/031,917 (Docket No. 6404P), 60/031,761 (Docket No. 6405P), 60/031,762 (Docket No. 6406P), 60/031,844 (Docket No. 6409P), No. 60/061,971, Attorney docket No 6881P October 14, 1997, No. 60/061,975, Attorney docket No 6882P October 14, 1997, No. 60/062,086, Attorney docket No 6883P October 14, 1997, No.

10 60/061,916, Attorney docket No 6884P October 14, 1997, No. 60/061,970, Attorney docket No 6885P October 14, 1997, No. 60/062,407, Attorney docket No 6886P October 14, 1997, 60/053,319 filed on July 21 1997 (Docket No. 6766P), 60/053,318 filed on July 21 1997 (Docket No. 6767P), 60/053,321 filed on July 21 1997 (Docket No. 6768P), 60/053,209 filed on July 21 1997 (Docket No. 6769P), 60/053,328 filed on July 21 1997

15 (Docket No. 6770P), 60/053,186 filed on July 21 1997 (Docket No. 6771P), 60/053,437 filed on August 8 1997 (Docket No. 6796P), 60/105,017 filed on October 20 1998 (Docket No. 7303P), and 60/104,962 filed on October 20 1998 (Docket No. 7304P) all of which are incorporated herein by reference.

The compositions of the present invention preferably comprise from about 0.01% to about 55%, more preferably from about 0.1% to about 45%, more preferably from about 0.25% to about 30%, more preferably from about 0.5% to about 20%, by weight of co-surfactants. Selected co-surfactants are further identified as follows.

(1) Anionic Co-surfactants:

Nonlimiting examples of anionic co-surfactants useful herein, typically at levels from about 0.1% to about 50%, by weight, include the conventional C₁₁-C₁₈ alkyl benzene sulfonates ("LAS") and primary, branched-chain and random C₁₀-C₂₀ alkyl sulfates ("AS"), the C₁₀-C₁₈ secondary (2,3) alkyl sulfates of the formula CH₃(CH₂)_x(CHOSO₃⁻M⁺)CH₃ and CH₃(CH₂)_y(CHOSO₃⁻M⁺)CH₂CH₃ where x and (y + 1) are integers of at least about 7, preferably at least about 9, and M is a

water-solubilizing cation, especially sodium, unsaturated sulfates such as oleyl sulfate, the C₁₀-C₁₈ alpha-sulfonated fatty acid esters, the C₁₀-C₁₈ sulfated alkyl polyglycosides, the C₁₀-C₁₈ alkyl alkoxy sulfates ("AE_xS"; especially EO 1-7 ethoxy sulfates), and C₁₀-C₁₈ alkyl alkoxy carboxylates (especially the EO 1-5 ethoxycarboxylates). The C₁₂-C₁₈ betaines and sulfobetaines ("sultaines"), C₁₀-C₁₈ amine oxides, and the like, can also be included in the overall compositions. C₁₀-C₂₀ conventional soaps may also be used. If high sudsing is desired, the branched-chain C₁₀-C₁₆ soaps may be used. Other conventional useful anionic co-surfactants are listed in standard texts.

Other suitable anionic surfactants that can be used are alkyl ester sulfonate surfactants including linear esters of C₈-C₂₀ carboxylic acids (i.e., fatty acids) which are sulfonated with gaseous SO₃ according to "The Journal of the American Oil Chemists Society", 52 (1975), pp. 323-329. Suitable starting materials would include natural fatty substances as derived from tallow, palm oil, etc.

Another type of useful surfactants is the so-called dianionics. These are surfactants that have at least two anionic groups present on the surfactant molecule. Some suitable dianionic surfactants are further described in copending U.S. Serial No. 60/020,503 (Docket No. 6160P), 60/020,772 (Docket No. 6161P), 60/020,928 (Docket No. 6158P), 60/020,832 (Docket No. 6159P) and 60/020,773 (Docket No. 6162P) all filed on June 28, 1996, and 60/023,539 (Docket No. 6192P), 60/023,493 (Docket No. 6194P), 60/023,540 (Docket No. 6193P) and 60/023,527 (Docket No. 6195P) filed on August 8th, 1996, the disclosures of which are incorporated herein by reference.

Additionally and preferably, the surfactant may be a branched alkyl sulfate, branched alkyl alkoxylate, or branched alkyl alkoxylate sulfate. These surfactants are further described in No. 60/061,971, Attorney docket No 6881P October 14, 1997, No. 60/061,975, Attorney docket No 6882P October 14, 1997, No. 60/062,086, Attorney docket No 6883P October 14, 1997, No. 60/061,916, Attorney docket No 6884P October 14, 1997, No. 60/061,970, Attorney docket No 6885P October 14, 1997, No. 60/062,407, Attorney docket No 6886P October 14, 1997,. Other suitable mid-chain branched surfactants can be found in U.S. Patent applications Serial Nos. 60/032,035 (Docket No.

6401P), 60/031,845 (Docket No. 6402P), 60/031,916 (Docket No. 6403P), 60/031,917 (Docket No. 6404P), 60/031,761 (Docket No. 6405P), 60/031,762 (Docket No. 6406P) and 60/031,844 (Docket No. 6409P). Mixtures of these branched surfactants with conventional linear surfactants are also suitable for use in the present compositions.

5 Additionally, the surfactant may be a modified alkylbenzene sulfonate surfactants, or MLAS. Suitable MLAS surfactants can be found in U.S. Patent applications Serial Nos. 60/053,319 filed on July 21 1997 (Docket No. 6766P), 60/053,318 filed on July 21 1997 (Docket No. 6767P), 60/053,321 filed on July 21 1997 (Docket No. 6768P), 60/053,209 filed on July 21 1997 (Docket No. 6769P), 60/053,328 filed on July 21 1997 (Docket No. 6770P), 60/053,186 filed on July 21 1997 (Docket No. 6771P), 60/053,437 filed on August 8 1997 (Docket No. 6796P), 60/105,017 filed on October 20 1998 (Docket No. 7303P), and 60/104,962 filed on October 20 1998 (Docket No. 7304P). Mixtures of these branched surfactants with conventional linear surfactants are also suitable for use in the present compositions.

15 The anionic surfactants useful in the LDL of the present invention are preferably selected from the group consisting of, linear alkylbenzene sulfonate, alpha olefin sulfonate, paraffin sulfonates, alkyl ester sulfonates, alkyl sulfates, alkyl alkoxy sulfate, alkyl sulfonates, alkyl alkoxy carboxylate, alkyl alkoxyated sulfates, sarcosinates, taurinates, and mixtures thereof. An effective amount, typically from about 0.5% to about 20 90%, preferably about 5% to about 50%, more preferably from about 10 to about 30%, by weight of anionic detergent surfactant can be used in the LDL compositions of the present invention.

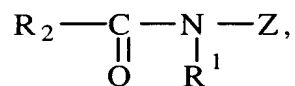
When included therein, the laundry detergent compositions of the present invention typically comprise from about 0.1% to about 50%, preferably from about 1% to 25 about 40% by weight of an anionic surfactant.

(2) Nonionic Co-surfactants:

Nonlimiting examples of nonionic co-surfactants useful herein typically at levels from about 0.1% to about 50%, by weight include the alkoxyated alcohols (AE's) and alkyl phenols, polyhydroxy fatty acid amides (PFAA's), alkyl polyglycosides (APG's), 30 C₁₀-C₁₈ glycerol ethers, and the like.

Examples of commercially available nonionic surfactants of this type include: TergitolTM 15-S-9 (the condensation product of C₁₁-C₁₅ linear alcohol with 9 moles ethylene oxide) and TergitolTM 24-L-6 NMW (the condensation product of C₁₂-C₁₄ primary alcohol with 6 moles ethylene oxide with a narrow molecular weight distribution), both marketed by Union Carbide Corporation; NeodolTM 45-9 (the condensation product of C₁₄-C₁₅ linear alcohol with 9 moles of ethylene oxide), NeodolTM 23-3 (the condensation product of C₁₂-C₁₃ linear alcohol with 3 moles of ethylene oxide), NeodolTM 45-7 (the condensation product of C₁₄-C₁₅ linear alcohol with 7 moles of ethylene oxide) and NeodolTM 45-5 (the condensation product of C₁₄-C₁₅ linear alcohol with 5 moles of ethylene oxide) marketed by Shell Chemical Company; KyroTM EOB (the condensation product of C₁₃-C₁₅ alcohol with 9 moles ethylene oxide), marketed by The Procter & Gamble Company; and Genapol LA O3O or O5O (the condensation product of C₁₂-C₁₄ alcohol with 3 or 5 moles of ethylene oxide) marketed by Hoechst. The preferred range of HLB in these AE nonionic surfactants is from 8-17 and most preferred from 8-14. Condensates with propylene oxide and butylene oxides may also be used.

Another class of preferred nonionic co-surfactants for use herein are the polyhydroxy fatty acid amide surfactants of the formula.



wherein R¹ is H, or C₁₋₄ hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl or a mixture thereof, R² is C₅₋₃₁ hydrocarbyl, and Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxyated derivative thereof. Typical examples include the C₁₂-C₁₈ and C₁₂-C₁₄ N-methylglucamides. See U.S. 5,194,639 and 5,298,636. N-alkoxy polyhydroxy fatty acid amides can also be used; see U.S. 5,489,393.

Also useful as a nonionic co-surfactant in the present invention are the alkylpolysaccharides such as those disclosed in U.S. Patent 4,565,647, Llenado, issued January 21, 1986.

Preferred alkylpolyglycosides have the formula



wherein R^2 is selected from the group consisting of alkyl, alkylphenyl, hydroxyalkyl, hydroxyalkylphenyl, and mixtures thereof in which the alkyl groups contain from about 10 to about 18, preferably from about 12 to about 14, carbon atoms; n is 2 or 3, preferably 2; t is from 0 to about 10, preferably 0; and x is from about 1.3 to about 10, preferably from about 1.3 to about 3, most preferably from about 1.3 to about 2.7. The glycosyl is preferably derived from glucose. To prepare these compounds, the alcohol or alkylpolyethoxy alcohol is formed first and then reacted with glucose, or a source of glucose, to form the glucoside (attachment at the 1-position). The additional glycosyl units can then be attached between their 1-position and the preceding glycosyl units 2-, 3-, 10 4- and/or 6-position, preferably predominately the 2-position. Compounds of this type and their use in detergent are disclosed in EP-B 0 070 077, 0 075 996 and 0 094 118.

Polyethylene, polypropylene, and polybutylene oxide condensates of alkyl phenols are also suitable for use as the nonionic surfactant of the surfactant systems of the present invention, with the polyethylene oxide condensates being preferred. These compounds 20 include the condensation products of alkyl phenols having an alkyl group containing from about 6 to about 14 carbon atoms, preferably from about 8 to about 14 carbon atoms, in either a straight-chain or branched-chain configuration with the alkylene oxide. In a preferred embodiment, the ethylene oxide is present in an amount equal to from about 2 to about 25 moles, more preferably from about 3 to about 15 moles, of ethylene oxide per 25 mole of alkyl phenol. Commercially available nonionic surfactants of this type include IgepalTM CO-630, marketed by the GAF Corporation; and TritonTM X-45, X-114, X-100 and X-102, all marketed by the Rohm & Haas Company. These surfactants are commonly referred to as alkylphenol alkoxylates (e.g., alkyl phenol ethoxylates).

The condensation products of ethylene oxide with a hydrophobic base formed by 30 the condensation of propylene oxide with propylene glycol are also suitable for use as the

additional nonionic surfactant in the present invention. The hydrophobic portion of these compounds will preferably have a molecular weight of from about 1500 to about 1800 and will exhibit water insolubility. The addition of polyoxyethylene moieties to this hydrophobic portion tends to increase the water solubility of the molecule as a whole, and the liquid character of the product is retained up to the point where the polyoxyethylene content is about 50% of the total weight of the condensation product, which corresponds to condensation with up to about 40 moles of ethylene oxide. Examples of compounds of this type include certain of the commercially-available PluronicTM surfactants, marketed by BASF.

Also suitable for use as the nonionic surfactant of the nonionic surfactant system of the present invention, are the condensation products of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylenediamine. The hydrophobic moiety of these products consists of the reaction product of ethylenediamine and excess propylene oxide, and generally has a molecular weight of from about 2500 to about 3000. This hydrophobic moiety is condensed with ethylene oxide to the extent that the condensation product contains from about 40% to about 80% by weight of polyoxyethylene and has a molecular weight of from about 5,000 to about 11,000. Examples of this type of nonionic surfactant include certain of the commercially available TetronicTM compounds, marketed by BASF.

When the composition is an automatic dishwashing composition (ADW), it preferably contains a nonionic co-surfactants. In general, bleach-stable nonionic co-surfactants are preferred. These nonionic co-surfactants when present, are included at levels of from about 0.1% to about 15% of the composition. The nonionic co-surfactant may be a low cloud point nonionic co-surfactant, a high cloud point nonionic co-surfactant or mixtures thereof. One preferred ADW composition of the present invention, includes a low cloud point nonionic co-surfactant, and/or a high cloud point nonionic co-surfactant in addition to the surfactant of the present invention. Nonionic surfactants generally are well known, being described in more detail in Kirk Othmer's Encyclopedia of Chemical Technology, 3rd Ed., Vol. 22, pp. 360-379, "Surfactants and Detergent Systems", incorporated by reference herein.

"Cloud point", as used herein, is a well known property of nonionic surfactants which is the result of the surfactant becoming less soluble with increasing temperature, the temperature at which the appearance of a second phase is observable is referred to as the "cloud point" (See Kirk Othmer, pp. 360-362, hereinbefore).

5 As used herein, a "low cloud point" nonionic co-surfactant is defined as a nonionic surfactant system ingredient having a cloud point of less than 30°C, preferably less than about 20°C, and most preferably less than about 10°C. Typical low cloud point nonionic co-surfactants include nonionic alkoxyated surfactants, especially ethoxylates derived from primary alcohol, and polyoxypropylene/polyoxyethylene/polyoxypropylene
10 (PO/EO/PO) reverse block polymers. Also, such low cloud point nonionic co-surfactants include, for example, ethoxylated-propoxylated alcohol (e.g., Olin Corporation's Poly-Tergent® SLF18) and epoxy-capped poly(oxyalkylated) alcohols (e.g., Olin Corporation's Poly-Tergent® SLF18B series of nonionics, as described, for example, in WO 94/22800, published October 13, 1994 by Olin Corporation).

15 Nonionic co-surfactants can optionally contain propylene oxide in an amount up to about 15% by weight. Other preferred nonionic co-surfactants can be prepared by the processes described in U.S. Patent 4,223,163, issued September 16, 1980, Builloty, incorporated herein by reference.

Low cloud point nonionic co-surfactants additionally comprise a polyoxyethylene,
20 polyoxypropylene block polymeric compound. Block polyoxyethylene-polyoxypropylene polymeric compounds include those based on ethylene glycol, propylene glycol, glycerol, trimethylolpropane and ethylenediamine as initiator reactive hydrogen compound. Certain of the block polymer surfactant compounds designated PLURONIC®, REVERSED PLURONIC®, and TETRONIC® by the BASF-Wyandotte Corp.,
25 Wyandotte, Michigan, are suitable in ADD compositions of the invention. Preferred examples include REVERSED PLURONIC® 25R2 and TETRONIC® 702. Such co-surfactants are typically useful herein as low cloud point nonionic surfactants.

As used herein, a "high cloud point" nonionic co-surfactant is defined as a nonionic surfactant system ingredient having a cloud point of greater than 40°C,
30 preferably greater than about 50°C, and more preferably greater than about 60°C.

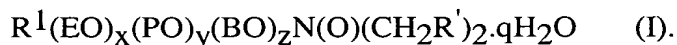
Preferably the nonionic co-surfactant system comprises an ethoxylated surfactant derived from the reaction of a monohydroxy alcohol or alkylphenol containing from about 8 to about 20 carbon atoms, with from about 6 to about 15 moles of ethylene oxide per mole of alcohol or alkyl phenol on an average basis. Such high cloud point nonionic co-surfactants include, for example, Tergitol 15S9 (supplied by Union Carbide), Rhodasurf TMD 8.5 (supplied by Rhone Poulenc), and Neodol 91-8 (supplied by Shell).

It is also preferred for purposes of the present invention that the high cloud point nonionic co-surfactant further have a hydrophile-lipophile balance ("HLB"; see Kirk Othmer hereinbefore) value within the range of from about 9 to about 15, preferably 11 to 15. Such materials include, for example, Tergitol 15S9 (supplied by Union Carbide), Rhodasurf TMD 8.5 (supplied by Rhone Poulenc), and Neodol 91-8 (supplied by Shell).

Another preferred high cloud point nonionic co-surfactant is derived from a straight or preferably branched chain or secondary fatty alcohol containing from about 6 to about 20 carbon atoms (C₆-C₂₀ alcohol), including secondary alcohols and branched chain primary alcohols. Preferably, high cloud point nonionic co-surfactants are branched or secondary alcohol ethoxylates, more preferably mixed C9/11 or C11/15 branched alcohol ethoxylates, condensed with an average of from about 6 to about 15 moles, preferably from about 6 to about 12 moles, and most preferably from about 6 to about 9 moles of ethylene oxide per mole of alcohol. Preferably the ethoxylated nonionic co-surfactant so derived has a narrow ethoxylate distribution relative to the average.

When the optional co-surfactants are a mixture of low cloud point nonionics and high cloud point nonionics it is preferred that the mixture is combined in a weight ratio preferably within the range of from about 10:1 to about 1:10.

Also preferred nonionics are amine oxide surfactants. The compositions of the present invention may comprise amine oxide in accordance with the general formula I:



In general, it can be seen that the structure (I) provides one long-chain moiety $R^1(EO)_x(PO)_y(BO)_z$ and two short chain moieties, CH_2R' . R' is preferably selected from hydrogen, methyl and $-CH_2OH$. In general R^1 is a primary or branched hydrocarbyl

moiety which can be saturated or unsaturated, preferably, R^1 is a primary alkyl moiety. When $x+y+z = 0$, R^1 is a hydrocarbyl moiety having chainlength of from about 8 to about 18. When $x+y+z$ is different from 0, R^1 may be somewhat longer, having a chainlength in the range C_{12} - C_{24} . The general formula also encompasses amine oxides wherein

5 $x+y+z = 0$, $R_1 = C_8$ - C_{18} , $R' = H$ and $q = 0$ -2, preferably 2. These amine oxides are illustrated by C_{12} - C_{14} alkyldimethyl amine oxide, tetradecyldimethylamine oxide, hexadecyl dimethylamine oxide, octadecylamine oxide and their hydrates, especially the dihydrates as disclosed in U.S. Patents 5,075,501 and 5,071,594, incorporated herein by reference.

10 The invention also encompasses amine oxides wherein $x+y+z$ is different from zero, specifically $x+y+z$ is from about 1 to about 10, R^1 is a primary alkyl group containing 8 to about 24 carbons, preferably from about 12 to about 16 carbon atoms; in these embodiments $y + z$ is preferably 0 and x is preferably from about 1 to about 6, more preferably from about 2 to about 4; EO represents ethyleneoxy; PO represents

15 propyleneoxy; and BO represents butyleneoxy. Such amine oxides can be prepared by conventional synthetic methods, e.g., by the reaction of alkylethoxysulfates with dimethylamine followed by oxidation of the ethoxylated amine with hydrogen peroxide.

Highly preferred amine oxides herein are solutions at ambient temperature. Amine oxides suitable for use herein are made commercially by a number of suppliers, including

20 Akzo Chemie, Ethyl Corp., and Procter & Gamble. See McCutcheon's compilation and Kirk-Othmer review article for alternate amine oxide manufacturers.

Whereas in certain of the preferred embodiments R' is H, there is some latitude with respect to having R' slightly larger than H. Specifically, the invention further encompasses embodiments wherein R' is CH_2OH , such as hexadecylbis(2-

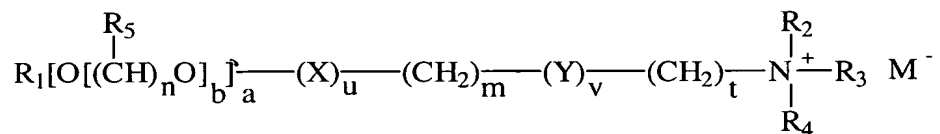
25 hydroxyethyl)amine oxide, tallowbis(2-hydroxyethyl)amine oxide, stearylbis(2-hydroxyethyl)amine oxide and oleylbis(2-hydroxyethyl)amine oxide, dodecyldimethylamine oxide dihydrate.

(3) Cationic Co-surfactants:

Nonlimiting examples of cationic co-surfactants useful herein typically at levels from about 0.1% to about 50%, by weight include the choline ester-type quats and alkoxylated quaternary ammonium (AQA) surfactant compounds, and the like. Most preferred for aqueous liquid compositions herein are soluble cationic co-surfactants which do not readily hydrolyze in the product.

Cationic co-surfactants useful as a component of the surfactant system is a cationic choline ester-type quat surfactant which are preferably water dispersible compounds having surfactant properties and comprise at least one ester (i.e. -COO-) linkage and at least one cationically charged group. Suitable cationic ester surfactants, including choline ester surfactants, have for example been disclosed in U.S. Patents Nos. 4,228,042, 4,239,660 and 4,260,529.

Cationic ester surfactants include those having the formula:

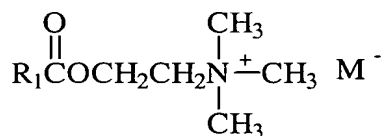


wherein R_1 is a C_5 - C_{31} linear or branched alkyl, alkenyl or alkaryl chain or M^- $N^+(R_6R_7R_8)(CH_2)_5$; X and Y, independently, are selected from the group consisting of COO, OCO, O, CO, OCOO, CONH, NHCO, OCONH and NHCOO wherein at least one of X or Y is a COO, OCO, OCOO, OCONH or NHCOO group; R_2 , R_3 , R_4 , R_6 , R_7 and R_8 are independently selected from the group consisting of alkyl, alkenyl, hydroxyalkyl, hydroxyalkenyl and alkaryl groups having from 1 to 4 carbon atoms; and R_5 is independently H or a C_1 - C_3 alkyl group; wherein the values of m, n, s and t independently lie in the range of from 0 to 8, the value of b lies in the range from 0 to 20, and the values of a, u and v independently are either 0 or 1 with the proviso that at least one of u or v must be 1; and wherein M is a counter anion.

Preferably R_2 , R_3 and R_4 are independently selected from CH_3 and $-CH_2CH_2OH$.

Preferably M is selected from the group consisting of halide, methyl sulfate, sulfate, and nitrate, more preferably methyl sulfate, chloride, bromide or iodide.

Preferred water dispersible cationic ester surfactants are the choline esters having the formula:



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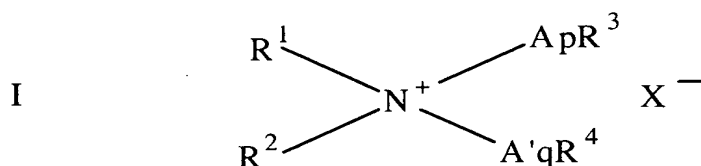
wherein R₁ is a C₁₁-C₁₉ linear or branched alkyl chain.

Particularly preferred choline esters of this type include the stearoyl choline ester quaternary methylammonium halides (R¹=C₁₇ alkyl), palmitoyl choline ester quaternary methylammonium halides (R¹=C₁₅ alkyl), myristoyl choline ester quaternary methylammonium halides (R¹=C₁₃ alkyl), lauroyl choline ester quaternary methylammonium halides (R¹=C₁₁ alkyl), cocoyl choline ester quaternary methylammonium halides (R¹=C₁₁-C₁₃ alkyl), tallowyl choline ester quaternary methylammonium halides (R¹=C₁₅-C₁₇ alkyl), and any mixtures thereof.

The particularly preferred choline esters, given above, may be prepared by the direct esterification of a fatty acid of the desired chain length with dimethylaminoethanol, in the presence of an acid catalyst. The reaction product is then quaternized with a methyl halide, preferably in the presence of a solvent such as ethanol, propylene glycol or preferably a fatty alcohol ethoxylate such as C₁₀-C₁₈ fatty alcohol ethoxylate having a degree of ethoxylation of from 3 to 50 ethoxy groups per mole forming the desired cationic material. They may also be prepared by the direct esterification of a long chain fatty acid of the desired chain length together with 2-haloethanol, in the presence of an acid catalyst material. The reaction product is then quaternized with trimethylamine, forming the desired cationic material.

In a preferred aspect these cationic ester surfactant are hydrolysable under the conditions of a laundry wash method.

Cationic co-surfactants useful herein also include alkoxyated quaternary ammonium (AQA) surfactant compounds (referred to hereinafter as "AQA compounds") having the formula:



5

wherein R^1 is an alkyl or alkenyl moiety containing from about 8 to about 18 carbon atoms, preferably 10 to about 16 carbon atoms, most preferably from about 10 to about 14 carbon atoms; R^2 is an alkyl group containing from one to three carbon atoms, preferably methyl; R^3 and R^4 can vary independently and are selected from hydrogen (preferred), methyl and ethyl; X^- is an anion such as chloride, bromide, methylsulfate, sulfate, or the like, sufficient to provide electrical neutrality. A and A' can vary independently and are each selected from C_1 - C_4 alkoxy, especially ethoxy (i.e., $-\text{CH}_2\text{CH}_2\text{O}-$), propoxy, butoxy and mixed ethoxy/propoxy; p is from 0 to about 30, preferably 1 to about 4 and q is from 0 to about 30, preferably 1 to about 4, and most preferably to about 4; preferably both p and q are 1. See also: EP 2,084, published May 30, 1979, by The Procter & Gamble Company, which describes cationic co-surfactants of this type which are also useful herein..

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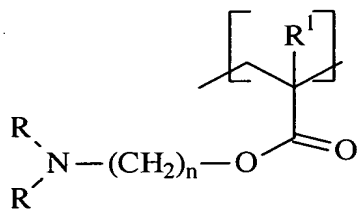
The levels of the AQA surfactants used to prepare finished laundry detergent compositions typically range from about 0.1% to about 5%, preferably from about 0.45% to about 2.5%, by weight.

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Polymeric Suds Stabilizer - The compositions of the present invention may optionally contain a polymeric suds stabilizer. These polymeric suds stabilizers provide extended suds volume and suds duration without sacrificing the grease cutting ability of the liquid detergent compositions. These polymeric suds stabilizers are selected from:

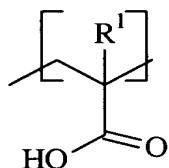
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- i) homopolymers of (N,N-dialkylamino)alkyl acrylate esters having the formula:



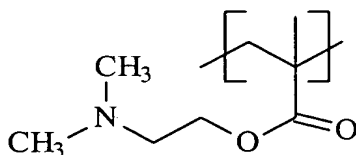
wherein each R is independently hydrogen, C₁-C₈ alkyl, and mixtures thereof, R¹ is hydrogen, C₁-C₆ alkyl, and mixtures thereof, n is from 2 to about 6; and

ii) copolymers of (i) and



wherein R¹ is hydrogen, C₁-C₆ alkyl, and mixtures thereof, provided that the ratio of (ii) to (i) is from about 2 to 1 to about 1 to 2; The molecular weight of the polymeric suds boosters, determined via conventional gel permeation chromatography, is from about 1,000 to about 2,000,000, preferably from about 5,000 to about 1,000,000, more preferably from about 10,000 to about 750,000, more preferably from about 20,000 to about 500,000, even more preferably from about 35,000 to about 200,000. The polymeric suds stabilizer can optionally be present in the form of a salt, either an inorganic or organic salt, for example the citrate, sulfate, or nitrate salt of (N,N-dimethylamino)alkyl acrylate ester.

One preferred polymeric suds stabilizer is (N,N-dimethylamino)alkyl acrylate esters, namely



When present in the compositions, the polymeric suds booster may be present in the composition from about 0.01% to about 15%, preferably from about 0.05% to about 10%, more preferably from about 0.1% to about 5%, by weight.

Other suitable polymeric suds stabilizers, including protenacious suds stabilizers and zwitterionic suds stabilizers, can be found in PCT/US98/24853 filed November 20, 1998 (Docket No. 6938), PCT/US98/24707 filed November 20, 1998 (Docket No. 6939), PCT/US98/24699 filed November 20, 1998 (Docket No. 6943), and PCT/US98/24852 filed November 20, 1998 (Docket No. 6944). Also suitable are the cationic copolymer stabilizers, which can be found in US Patent 4454060.

Enzymes - Detergent compositions of the present invention may further comprise one or more enzymes which provide cleaning performance benefits. Said enzymes include enzymes selected from cellulases, hemicellulases, peroxidases, proteases, glucosylases, amylases, lipases, cutinases, pectinases, xylanases, reductases, oxidases, phenoloxidases, lipxygenases, ligninases, pullulanases, tannases, pentosanases, malanases, β -glucanases, arabinosidases or mixtures thereof. A preferred combination is a detergent composition having a cocktail of conventional applicable enzymes like protease, amylase, lipase, cutinase and/or cellulase. Enzymes when present in the compositions, at from about 0.0001% to about 5% of active enzyme by weight of the detergent composition.

Proteolytic Enzyme - The proteolytic enzyme can be of animal, vegetable or microorganism (preferred) origin. The proteases for use in the detergent compositions herein include (but are not limited to) trypsin, subtilisin, chymotrypsin and elastase-type proteases. Preferred for use herein are subtilisin-type proteolytic enzymes. Particularly preferred is bacterial serine proteolytic enzyme obtained from Bacillus subtilis and/or Bacillus licheniformis.

Suitable proteolytic enzymes include Novo Industri A/S Alcalase[®] (preferred), Esperase[®], Savinase[®] (Copenhagen, Denmark), Gist-brocades' Maxatase[®], Maxacal[®] and Maxapem 15[®] (protein engineered Maxacal[®]) (Delft, Netherlands), and subtilisin BPN and BPN' (preferred), which are commercially available. Preferred proteolytic enzymes are also modified bacterial serine proteases, such as those made by Genencor

International, Inc. (San Francisco, California) which are described in European Patent 251,446B, granted December 28, 1994 (particularly pages 17, 24 and 98) and which are also called herein "Protease B". U.S. Patent 5,030,378, Venegas, issued July 9, 1991, refers to a modified bacterial serine proteolytic enzyme (Genencor International) which is called "Protease A" herein (same as BPN'). In particular see columns 2 and 3 of U.S. Patent 5,030,378 for a complete description, including amino sequence, of Protease A and its variants. Other proteases are sold under the tradenames: Primase, Durazym, Opticlean and Optimase. Preferred proteolytic enzymes, then, are selected from the group consisting of Alcalase [®] (Novo Industri A/S), BPN', Protease A and Protease B (Genencor), and mixtures thereof. Protease B is most preferred.

Of particular interest for use herein are the proteases described in U.S. Patent No. 5,470,733.

Also proteases described in our co-pending application USSN 08/136,797 can be included in the detergent composition of the invention.

Another preferred protease, referred to as "Protease D" is a carbonyl hydrolase variant having an amino acid sequence not found in nature, which is derived from a precursor carbonyl hydrolase by substituting a different amino acid for a plurality of amino acid residues at a position in said carbonyl hydrolase equivalent to position +76, preferably also in combination with one or more amino acid residue positions equivalent to those selected from the group consisting of +99, +101, +103, +104, +107, +123, +27, +105, +109, +126, +128, +135, +156, +166, +195, +197, +204, +206, +210, +216, +217, +218, +222, +260, +265, and/or +274 according to the numbering of Bacillus amyloliquefaciens subtilisin, as described in WO 95/10615 published April 20, 1995 by Genencor International (A. Baeck et al. entitled "Protease-Containing Cleaning Compositions" having U.S. Serial No. 08/322,676, filed October 13, 1994).

Useful proteases are also described in PCT publications: WO 95/30010 published November 9, 1995 by The Procter & Gamble Company; WO 95/30011 published November 9, 1995 by The Procter & Gamble Company; WO 95/29979 published November 9, 1995 by The Procter & Gamble Company.

Protease enzyme may be incorporated into the compositions in accordance with the invention at a level of from 0.0001% to 2% active enzyme by weight of the composition.

Amylase - Amylases (α and/or β) can be included for removal of carbohydrate-based stains. Suitable amylases are Termamyl® (Novo Nordisk), Fungamyl® and BAN® (Novo Nordisk). The enzymes may be of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. Amylase enzymes are normally incorporated in the detergent composition at levels from 0.0001% to 2%, preferably from about 0.0001% to about 0.5%, more preferably from about 0.0005% to about 0.1%, even more preferably from about 0.001% to about 0.05% of active enzyme by weight of the detergent composition.

Amylase enzymes also include those described in WO95/26397 and in co-pending application by Novo Nordisk PCT/DK96/00056.

One suitable amylase enzyme is NATALASE® available from Novo Nordisk.

Other amylases suitable herein include, for example, α -amylases described in GB 1,296,839 to Novo; RAPIDASE®, International Bio-Synthetics, Inc. and TERMAMYL®, Novo. FUNGAMYL® from Novo is especially useful.

Particularly preferred amylases herein include amylase variants having additional modification in the immediate parent as described in WO 9510603 A and are available from the assignee, Novo, as DURAMYL®. Other particularly preferred oxidative stability enhanced amylase include those described in WO 9418314 to Genencor International and WO 9402597 to Novo. Any other oxidative stability-enhanced amylase can be used, for example as derived by site-directed mutagenesis from known chimeric, hybrid or simple mutant parent forms of available amylases. Other preferred enzyme modifications are accessible. See WO 9509909 A to Novo.

Various carbohydrase enzymes which impart antimicrobial activity may also be included in the present invention. Such enzymes include endoglycosidase, Type II endoglycosidase and glucosidase as disclosed in U.S. Patent Nos. 5,041,236, 5,395,541, 5,238,843 and 5,356,803 the disclosures of which are herein incorporated by reference. Of course, other enzymes having antimicrobial activity may be employed as well including peroxidases, oxidases and various other enzymes.

It is also possible to include an enzyme stabilization system into the compositions of the present invention when any enzyme is present in the composition.

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10 of the present invention when any enzyme is present in the composition.

Peroxidase enzymes can be used in combination with oxygen sources, e.g., percarbonate, perborate, persulfate, hydrogen peroxide, etc. They are typically used for "solution bleaching," i.e. to prevent transfer of dyes or pigments removed from substrates during wash operations to other substrates in the wash solution. Peroxidase enzymes are
15 known in the art, and include, for example, horseradish peroxidase, ligninase, and haloperoxidase such as chloro- and bromo-peroxidase. Peroxidase-containing detergent compositions are disclosed, for example, in PCT International Application WO 89/099813, published October 19, 1989, by O. Kirk, assigned to Novo Industries A/S. The present invention encompasses peroxidase-free automatic dishwashing composition
20 embodiments.

A wide range of enzyme materials and means for their incorporation into synthetic detergent compositions are also disclosed in U.S. Patent 3,553,139, issued January 5, 1971 to McCarty et al. Enzymes are further disclosed in U.S. Patent 4,101,457, Place et al, issued July 18, 1978, and in U.S. Patent 4,507,219, Hughes, issued March 26, 1985.
25 Enzymes for use in detergents can be stabilized by various techniques. Enzyme stabilization techniques are disclosed and exemplified in U.S. Patent 3,600,319, issued August 17, 1971 to Gedge, et al, and European Patent Application Publication No. 0 199 405, Application No. 86200586.5, published October 29, 1986, Venegas. Enzyme stabilization systems are also described, for example, in U.S. Patent 3,519,570.

The enzymes may be incorporated into detergent compositions herein in the form of suspensions, "marumes" or "prills". Another suitable type of enzyme comprises those in the form of slurries of enzymes in nonionic surfactants, e.g., the enzymes marketed by Novo Nordisk under the tradename "SL" or the microencapsulated enzymes marketed by
5 Novo Nordisk under the tradename "LDP."

Enzymes added to the compositions herein in the form of conventional enzyme prills are especially preferred for use herein. Such prills will generally range in size from about 100 to 1,000 microns, more preferably from about 200 to 800 microns and will be suspended throughout the non-aqueous liquid phase of the composition. Prills in the
10 compositions of the present invention have been found, in comparison with other enzyme forms, to exhibit especially desirable enzyme stability in terms of retention of enzymatic activity over time. Thus, compositions which utilize enzyme prills need not contain conventional enzyme stabilizing such as must frequently be used when enzymes are incorporated into aqueous liquid detergents.

15 If employed, enzymes will normally be incorporated into the non-aqueous liquid compositions herein at levels sufficient to provide up to about 10 mg by weight, more typically from about 0.01 mg to about 5 mg, of active enzyme per gram of the composition. Stated otherwise, the non-aqueous liquid detergent compositions herein will typically comprise from about 0.001% to 5%, preferably from about 0.01% to 1% by
20 weight, of a commercial enzyme preparation. Protease enzymes, for example, are usually present in such commercial preparations at levels sufficient to provide from 0.005 to 0.1 Anson units (AU) of activity per gram of composition.

Enzyme Stabilizing System - The enzyme-containing compositions herein may optionally also comprise from about 0.001% to about 10%, preferably from about 0.005%
25 to about 8%, most preferably from about 0.01% to about 6%, by weight of an enzyme stabilizing system. The enzyme stabilizing system can be any stabilizing system which is compatible with the deterative enzyme. Such a system may be inherently provided by other formulation actives, or be added separately, e.g., by the formulator or by a manufacturer of detergent-ready enzymes. Such stabilizing systems can, for example,
30 comprise calcium ion, boric acid, propylene glycol, short chain carboxylic acids, boronic

acids, and mixtures thereof, and are designed to address different stabilization problems depending on the type and physical form of the detergent composition.

Perfumes - Perfumes and perfumery ingredients useful in the present compositions and processes comprise a wide variety of natural and synthetic chemical ingredients, including, but not limited to, aldehydes, ketones, esters, and the like. Also included are various natural extracts and essences which can comprise complex mixtures of ingredients, such as orange oil, lemon oil, rose extract, lavender, musk, patchouli, balsamic essence, sandalwood oil, pine oil, cedar, and the like. Finished perfumes can comprise extremely complex mixtures of such ingredients. Finished perfumes typically
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comprise from about 0.01% to about 2%, by weight, of the detergent compositions herein, and individual perfumery ingredients can comprise from about 0.0001% to about 90% of a finished perfume composition.

Dispersant Polymer - The compositions of the present invention may additionally contain a dispersant polymer. When present, a dispersant polymer in the instant
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compositions is typically at levels in the range from 0 to about 25%, preferably from about 0.5% to about 20%, more preferably from about 1% to about 8% by weight of the composition. Dispersant polymers are useful for improved filming performance of the present compositions, especially in higher pH embodiments, such as those in which wash pH exceeds about 9.5. Particularly preferred are polymers which inhibit the deposition of
20
calcium carbonate or magnesium silicate on dishware.

Dispersant polymers suitable for use herein are further illustrated by the film-forming polymers described in U.S. Pat. No. 4,379,080 (Murphy), issued Apr. 5, 1983.

Suitable polymers are preferably at least partially neutralized or alkali metal, ammonium or substituted ammonium (e.g., mono-, di- or triethanolammonium) salts of
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polycarboxylic acids. The alkali metal, especially sodium salts are most preferred. While the molecular weight of the polymer can vary over a wide range, it preferably is from about 1,000 to about 500,000, more preferably is from about 1,000 to about 250,000, and most preferably, especially if the composition is for use in North American automatic dishwashing appliances, is from about 1,000 to about 5,000.

Sub
SA
A

Other suitable dispersant polymers include those disclosed in U.S. Pat. Nos. 3,308,067, 4,530,766, 3,723,322, 3,929,107, 3,803,285, 3,629,121, 4,141,841, and 5,084,535; EP Pat. No. 66,915,.

5 Copolymers of acrylamide and acrylate having a molecular weight of from about 3,000 to about 100,000, preferably from about 4,000 to about 20,000, and an acrylamide content of less than about 50%, preferably less than about 20%, by weight of the dispersant polymer can also be used.

Particularly preferred dispersant polymers are low molecular weight modified polyacrylate copolymers.

10 Suitable low molecular weight polyacrylate dispersant polymer preferably has a molecular weight of less than about 15,000, preferably from about 500 to about 10,000, most preferably from about 1,000 to about 5,000. The most preferred polyacrylate copolymer for use herein has a molecular weight of about 3,500 and is the fully neutralized form of the polymer comprising about 70% by weight acrylic acid and about
15 30% by weight methacrylic acid.

Other dispersant polymers useful herein include the polyethylene glycols and polypropylene glycols having a molecular weight of from about 950 to about 30,000 which can be obtained from the Dow Chemical Company of Midland, Michigan.

Yet other dispersant polymers useful herein include the cellulose sulfate esters such
20 as cellulose acetate sulfate, cellulose sulfate, hydroxyethyl cellulose sulfate, methylcellulose sulfate, and hydroxypropylcellulose sulfate. Sodium cellulose sulfate is the most preferred polymer of this group.

Yet another group of acceptable dispersants are the organic dispersant polymers, such as polyaspartate.

25 Material Care Agents - When the compositions of the present invention are automatic dishwashing compositions they may contain one or more material care agents which are effective as corrosion inhibitors and/or anti-tarnish aids. Such materials are preferred components of machine dishwashing compositions especially in certain European countries where the use of electroplated nickel silver and sterling silver is still
30 comparatively common in domestic flatware, or when aluminium protection is a concern

and the composition is low in silicate. Generally, such material care agents include metasilicate, silicate, bismuth salts, manganese salts, paraffin, triazoles, pyrazoles, thiols, mercaptans, aluminium fatty acid salts, and mixtures thereof.

When present, such protecting materials are preferably incorporated at low levels, e.g., from about 0.01% to about 5% of the composition. Suitable corrosion inhibitors include paraffin oil, typically a predominantly branched aliphatic hydrocarbon having a number of carbon atoms in the range of from about 20 to about 50; preferred paraffin oil is selected from predominantly branched C₂₅₋₄₅ species with a ratio of cyclic to noncyclic hydrocarbons of about 32:68. A paraffin oil meeting those characteristics is sold by Wintershall, Salzbergen, Germany, under the trade name WINOG 70. Additionally, the addition of low levels of bismuth nitrate (i.e., Bi(NO₃)₃) is also preferred.

Other corrosion inhibitor compounds include benzotriazole and comparable compounds; mercaptans or thiols including thionaphthol and thioanthranol; and finely divided Aluminium fatty acid salts, such as aluminium tristearate. The formulator will recognize that such materials will generally be used judiciously and in limited quantities so as to avoid any tendency to produce spots or films on glassware or to compromise the bleaching action of the compositions. For this reason, mercaptan anti-tarnishes which are quite strongly bleach-reactive and common fatty carboxylic acids which precipitate with calcium in particular are preferably avoided.

Chelating Agents - The detergent compositions herein may also optionally contain one or more iron and/or manganese chelating agents. Such chelating agents can be selected from the group consisting of amino carboxylates, amino phosphonates, polyfunctionally-substituted aromatic chelating agents and mixtures therein, all as hereinafter defined. Without intending to be bound by theory, it is believed that the benefit of these materials is due in part to their exceptional ability to remove iron and manganese ions from washing solutions by formation of soluble chelates.

Amino carboxylates useful as optional chelating agents include ethylenediaminetetracetates, N-hydroxyethylethylenediaminetriacetates, nitrilo-triacetates, ethylenediamine tetrapro-prionates, triethylenetetraaminehexacetates,

diethylenetriaminepentaacetates, and ethanoldi-glycines, alkali metal, ammonium, and substituted ammonium salts therein and mixtures therein.

Amino phosphonates are also suitable for use as chelating agents in the compositions of the invention when at least low levels of total phosphorus are permitted
5 in detergent compositions, and include ethylenediaminetetrakis (methylenephosphonates) as DEQUEST. Preferred, these amino phosphonates do not contain alkyl or alkenyl groups with more than about 6 carbon atoms.

Polyfunctionally-substituted aromatic chelating agents are also useful in the compositions herein. See U.S. Patent 3,812,044, issued May 21, 1974, to Connor et al.
10 Preferred compounds of this type in acid form are dihydroxydisulfobenzenes such as 1,2-dihydroxy-3,5-disulfobenzene.

A preferred biodegradable chelator for use herein is ethylenediamine disuccinate ("EDDS"), especially the [S,S] isomer as described in U.S. Patent 4,704,233, November 3, 1987, to Hartman and Perkins.

15 The compositions herein may also contain water-soluble methyl glycine diacetic acid (MGDA) salts (or acid form) as a chelant or co-builder. Similarly, the so called "weak" builders such as citrate can also be used as chelating agents.

If utilized, these chelating agents will generally comprise from about 0.1% to about 15% by weight of the detergent compositions herein. More preferably, if utilized,
20 the chelating agents will comprise from about 0.1% to about 3.0% by weight of such compositions.


Composition pH

The surfactants of the present invention may be used in compositions which cover a wide range, from acidic to basic and all shades in-between. The compositions of the
25 present invention can have a pH from 2 to 12. If a composition with a pH greater than 7 is to be more effective, it preferably should contain a buffering agent capable of providing a generally more alkaline pH in the composition and in dilute solutions, i.e., about 0.1% to 0.4% by weight aqueous solution, of the composition. The pKa value of this buffering agent should be about 0.5 to 1.0 pH units below the desired pH value of the composition
30 (determined as described above). Preferably, the pKa of the buffering agent should be

from about 7 to about 10. Under these conditions the buffering agent most effectively controls the pH while using the least amount thereof. Similarly, an acidic buffering system can be employed to maintain the compositions pH.

The buffering agent may be an active detergent in its own right, or it may be a low molecular weight, organic or inorganic material that is used in this composition solely for maintaining an alkaline pH. One type of preferred buffering agents for compositions of this invention are nitrogen-containing materials. Some examples are amino acids such as lysine or lower alcohol amines like mono-, di-, and tri-ethanolamine. Other preferred nitrogen-containing buffering agents are Tri(hydroxymethyl)amino methane (HOCH₂)₃CNH₃ (TRIS), 2-amino-2-ethyl-1,3-propanediol, 2-amino-2-methyl-propanol, 2-amino-2-methyl-1,3-propanol, disodium glutamate, N-methyl diethanolamide, 1,3-diamino-propanol N,N'-tetra-methyl-1,3-diamino-2-propanol, N,N-bis(2-hydroxyethyl)glycine (bicine) and N-tris (hydroxymethyl)methyl glycine (tricine). Mixtures of any of the above are also acceptable. Useful inorganic buffers/alkalinity sources include the alkali metal carbonates and alkali metal phosphates, e.g., sodium carbonate, sodium polyphosphate. Also suitable are organic acids like citric acid, acetic acid and the like. For additional buffers see McCutcheon's EMULSIFIERS AND DETERGENTS, North American Edition, 1997, McCutcheon Division, MC Publishing Company Kirk and WO 95/07971 both of which are incorporated herein by reference.

One highly preferred group of buffers, especially in LDL compositions, are diamines. Preferred organic diamines are those in which pK₁ and pK₂ are in the range of about 8.0 to about 11.5, preferably in the range of about 8.4 to about 11, even more preferably from about 8.6 to about 10.75. Preferred materials for performance and supply considerations are 1,3-bis(methylamine)-cyclohexane, 1,3 propane diamine (pK₁=10.5; pK₂=8.8), 1,6 hexane diamine (pK₁=11; pK₂=10), 1,3 pentane diamine (Dytek EP) (pK₁=10.5; pK₂=8.9), 2-methyl 1,5 pentane diamine (Dytek A) (pK₁=11.2; pK₂=10.0). Other preferred materials are the primary/primary diamines with alkylene spacers ranging from C₄ to C₈. In general, it is believed that primary diamines are preferred over secondary and tertiary diamines.

 Definition of pK1 and pK2 - As used herein, "pKa1" and "pKa2" are quantities of a type collectively known to those skilled in the art as "pKa". pKa is used herein in the same manner as is commonly known to people skilled in the art of chemistry. Values referenced herein can be obtained from literature, such as from "Critical Stability Constants: Volume 2, Amines" by Smith and Martell, Plenum Press, NY and London, 1975. Additional information on pKa's can be obtained from relevant company literature, such as information supplied by Dupont, a supplier of diamines. More detailed information of pKa's can be found in US Pat App No. 08/770,972 filed 12/29/96 to Procter & Gamble (Attorney Docket No. 6459)

Examples of preferred diamines include the following:
dimethyl aminopropyl amine, 1,6-hexane diamine, 1,3 propane diamine, 2-methyl 1,5 pentane diamine, 1,3-Pentanediamine, 1,3-diaminobutane, 1,2-bis(2-aminoethoxy)ethane, Isophorone diamine, 1,3-bis(methylamine)-cyclohexane and mixtures thereof.

The buffer can be complemented (i.e. for improved sequestration in hard water) by other optional detergency builder salts selected from nonphosphate detergency builders known in the art, which include the various water-soluble, alkali metal, ammonium or substituted ammonium borates, hydroxysulfonates, polyacetates, and polycarboxylates. Preferred are the alkali metal, especially sodium, salts of such materials. Alternate water-soluble, non-phosphorus organic builders can be used for their sequestering properties.

Examples of polyacetate and polycarboxylate builders are the sodium, potassium, lithium, ammonium and substituted ammonium salts of ethylenediamine tetraacetic acid; nitrilotriacetic acid, tartrate monosuccinic acid, tartrate disuccinic acid, oxydisuccinic acid, carboxymethoxysuccinic acid, mellitic acid, and sodium benzene polycarboxylate salts.

The buffering agent, if used, is present in the compositions of the invention herein at a level of from about 0.1% to 15%, preferably from about 1% to 10%, most preferably from about 2% to 8%, by weight of the composition. If the optional buffer used is a diamine, the composition will preferably contain at least about 0.1%, more preferably at least about 0.2%, even more preferably, at least about 0.25%, even more preferably still, at least about 0.5% by weight of said composition of diamine. The composition will also

preferably contain no more than about 15%, more preferably no more than about 10%, even more preferably, no more than about 6%, even more preferably, no more than about 5%, even more preferably still, no more than about 1.5% by weight of said composition of diamine.

5 Water-Soluble Silicates

The present compositions may further comprise water-soluble silicates. Water-soluble silicates herein are any silicates which are soluble to the extent that they do not adversely affect spotting/filming characteristics of the composition.

Examples of silicates are sodium metasilicate and, more generally, the alkali metal
 10 silicates, particularly those having a $\text{SiO}_2\text{:Na}_2\text{O}$ ratio in the range 1.6:1 to 3.2:1; and layered silicates, such as the layered sodium silicates described in U.S. Patent 4,664,839, issued May 12, 1987 to H. P. Rieck. NaSKS-6[®] is a crystalline layered silicate marketed by Hoechst (commonly abbreviated herein as "SKS-6"). Unlike zeolite builders, Na SKS-6 and other water-soluble silicates usefule herein do not contain aluminum. NaSKS-6 is
 15 the $\delta\text{-Na}_2\text{SiO}_5$ form of layered silicate and can be prepared by methods such as those described in German DE-A-3,417,649 and DE-A-3,742,043. SKS-6 is a preferred layered silicate for use herein, but other such layered silicates, such as those having the general formula $\text{NaMSi}_x\text{O}_{2x+1} \cdot y\text{H}_2\text{O}$ wherein M is sodium or hydrogen, x is a number from 1.9 to 4, preferably 2, and y is a number from 0 to 20, preferably 0 can be used. Various other
 20 layered silicates from Hoechst include NaSKS-5, NaSKS-7 and NaSKS-11, as the α -, β - and γ - forms. Other silicates may also be useful, such as for example magnesium silicate, which can serve as a crispening agent in granular formulations, as a stabilizing agent for oxygen bleaches, and as a component of suds control systems.

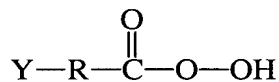
Silicates particularly useful in automatic dishwashing (ADD) applications include
 25 granular hydrous 2-ratio silicates such as BRITESIL[®] H20 from PQ Corp., and the commonly sourced BRITESIL[®] H24 though liquid grades of various silicates can be used when the ADD composition has liquid form. Within safe limits, sodium metasilicate or sodium hydroxide alone or in combination with other silicates may be used in an ADD context to boost wash pH to a desired level.

Bleaching Compounds

Bleaching Agents and Bleach Activators The compositions herein preferably further contain a bleach and/or a bleach activators. Bleaches agents will typically, when present, be at levels of from about 1% to about 30%, more typically from about 5% to about 20%,
 5 of the detergent composition, especially for fabric laundering. If present, the amount of bleach activators will typically be from about 0.1% to about 60%, more typically from about 0.5% to about 40% of the composition comprising the bleaching agent-plus-bleach activator.

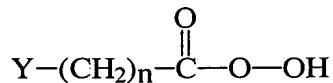
The bleaches used herein can be any of the bleaches useful for detergent
 10 compositions in textile cleaning, hard surface cleaning, or other cleaning purposes that are now known or become known. These include oxygen bleaches as well as other bleaching agents. Perborate bleaches, e.g., sodium perborate (e.g., mono- or tetra-hydrate) can be used herein. Also suitable are organic or inorganic peracids. Suitable organic or inorganic peracids for use herein include: percarboxylic acids and salts; percarbonic acids
 15 and salts; perimidic acids and salts; peroxymonosulfuric acids and salts; persulphates such as monopersulfate; peroxyacids such as diperoxydodecandioic acid (DPDA); magnesium perphthalic acid; perlauric acid; phthaloyl amidoperoxy caproic acid (PAP); perbenzoic and alkylperbenzoic acids; and mixtures thereof.

One class of suitable organic peroxydicarboxylic acids have the general
 20 formula:

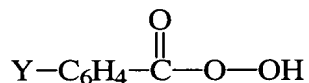


wherein R is an alkylene or substituted alkylene group containing from 1 to about 22 carbon atoms or a phenylene or substituted phenylene group, and Y is hydrogen, halogen, alkyl, aryl, -C(O)OH or -C(O)OOH.

25 Organic peroxyacids suitable for use in the present invention can contain either one or two peroxy groups and can be either aliphatic or aromatic. When the organic peroxydicarboxylic acid is aliphatic, the unsubstituted acid has the general formula:



where Y can be, for example, H, CH₃, CH₂Cl, C(O)OH, or C(O)OOH; and n is an integer from 1 to 20. When the organic peroxycarboxylic acid is aromatic, the unsubstituted acid has the general formula:



- 5 wherein Y can be, for example, hydrogen, alkyl, alkylhalogen, halogen, C(O)OH or C(O)OOH.

Typical monoperoxy acids useful herein include alkyl and aryl peroxyacids such as:

- 10 (i) peroxybenzoic acid and ring-substituted peroxybenzoic acid, e.g. peroxy-*a*-naphthoic acid, monoperoxyphthalic acid (magnesium salt hexahydrate), and *o*-carboxybenzamidoperoxyhexanoic acid (sodium salt);
- (ii) aliphatic, substituted aliphatic and arylalkyl monoperoxy acids, e.g. peroxyauric acid, peroxysearic acid, N-nonylaminoperoxypropionic acid (NAPCA), N,N-(3-octylsuccinoyl)aminoperoxypropionic acid (SAPA) and N,N-phthaloylaminoperoxypropionic acid (PAP);
- 15 (iii) amidoperoxyacids, e.g. monononylamide of either peroxysuccinic acid (NAPSA) or of peroxyadipic acid (NAPAA).

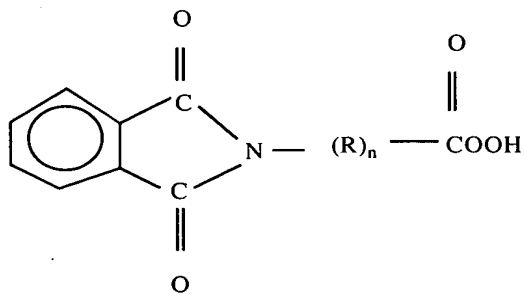
- Typical diperoxyacids useful herein include alkyl diperoxyacids and
- 20 aryldiperoxyacids, such as:

- (iv) 1,12-diperoxydodecanedioic acid;
- (v) 1,9-diperoxyazelaic acid;
- (vi) diperoxybrassylic acid; diperoxysebacic acid and diperoxyisophthalic acid;
- (vii) 2-decyldiperoxybutane-1,4-dioic acid;
- 25 (viii) 4,4'-sulfonylbis(2-peroxybenzoic acid).

Such bleaching agents are disclosed in U.S. Patent 4,483,781, Hartman, issued November 20, 1984, U.S. Patent 4,634,551 to Burns et al., European Patent Application 0,133,354, Banks et al. published February 20, 1985, and U.S. Patent 4,412,934, Chung et al. issued November 1, 1983. Sources also include 6-nonylamino-6-oxoperoxypropionic

acid as described in U.S. Patent 4,634,551, issued January 6, 1987 to Burns et al. Persulfate compounds such as for example OXONE, manufactured commercially by E.I. DuPont de Nemours of Wilmington, DE can also be employed as a suitable source of peroxymonosulfuric acid.

5 Particularly preferred peracid compounds are those having the formula:



wherein R is C₁₋₄ alkyl and n is an integer of from 1 to 5. A particularly preferred peracid has the formula where R is CH₂ and n is 5 i.e., phthaloylamino peroxy caproic acid (PAP) as described in U.S. Patent Nos. 5,487,818, 5,310,934, 5,246,620, 5,279,757 and
 10 5,132,431. PAP is available from Ausimont SpA under the tradename Euroco.

The peracids used herein preferably have a solubility in aqueous liquid compositions measured at 20 °C of from about 10 ppm to about 1500 ppm, more preferably from about 50 ppm to about 1000 ppm, most preferably from about 50 ppm to about 800 ppm solubility is measured at 20 °C.

15 In a particularly preferred embodiment of the present invention the peracid has mean average particle size of less than 100 microns, more preferably less than 80 microns, even more preferably less than 60 microns. Most preferably, when the peracid is PAP, it has a mean average particle size of between about 20 and about 50 microns.

Alternatively, although not preferred, the bleach can be a chlorine bleach.
 20 Chlorine bleaches can be any convenient conventional chlorine bleach. Such compounds are often divided in to two categories namely, inorganic chlorine bleaches and organic chlorine bleaches. Examples of the former are hypochlorites, such as sodium hypochlorite, calcium hypochlorite, potassium hypochlorite, magnesium hypochlorite. Another example of an inorganic chlorine bleach usable in the present invention is
 25 chlorinated trisodium phosphate dodecahydrate. Examples of the latter are isocyanurates,

such as potassium dichloroisocyanurate, sodium dichloroisocyanurate. Examples of other organic chlorine bleaches usable in the present invention are 1,3-dichloro-5,5-dimethylhydantoin, N-chlorosulfamide, chloramine T, Dichloramine T, chloramine B, Dichloramine T, N,N'-dichlorobenzoylene urea, paratoluene sulfondichoroamide, 5 trichloromethylamine, N-chloroammeline, N-chlorosuccinimide, N,N'-dichloroazodicarbonamide, N-chloroacetyl urea, N,N'-dichlorobiuret and chlorinated dicyandamide. Preferably the chlorine bleach is an inorganic chlorine bleach, more preferably it is sodium hypochlorite.

Another category of bleaches that can be used without restriction encompasses 10 percarboxylic acid bleaching agents and salts thereof. Suitable examples of this class of agents include magnesium monoperoxyphthalate hexahydrate, the magnesium salt of metachloro perbenzoic acid, 4-nonylamino-4-oxoperoxybutyric acid and diperoxydodecanedioic acid. Such bleaches are disclosed in U.S. Patent 4,483,781, Hartman, issued November 20, 1984, U.S. Patent Application 740,446, Burns et al, filed 15 June 3, 1985, European Patent Application 0,133,354, Banks et al, published February 20, 1985, and U.S. Patent 4,412,934, Chung et al, issued November 1, 1983. Highly preferred bleaches also include 6-nonylamino-6-oxoperoxy caproic acid as described in U.S. Patent 4,634,551, issued January 6, 1987 to Burns et al.

Peroxygen bleaches can also be used. Suitable peroxygen bleaching compounds 20 include sodium carbonate peroxyhydrate and equivalent "percarbonate" bleaches, sodium pyrophosphate peroxyhydrate, urea peroxyhydrate, and sodium peroxide. Persulfate bleach (e.g., OXONE, manufactured commercially by DuPont) can also be used.

A preferred percarbonate bleach comprises dry particles having an average particle size in the range from about 500 micrometers to about 1,000 micrometers, not more than 25 about 10% by weight of said particles being smaller than about 200 micrometers and not more than about 10% by weight of said particles being larger than about 1,250 micrometers. Optionally, the percarbonate can be coated with silicate, borate or water-soluble surfactants. Percarbonate is available from various commercial sources such as FMC, Solvay and Tokai Denka.

30 Mixtures of bleaches can also be used.

Peroxygen bleaches, the perborates, the percarbonates, etc., are preferably combined with bleach activators, which lead to the in situ production in aqueous solution (i.e., during the washing process) of the peroxy acid corresponding to the bleach activator. Various nonlimiting examples of activators are disclosed in U.S. Patent 4,915,854, issued
5 April 10, 1990 to Mao et al, and U.S. Patent 4,412,934. The nonanoyloxybenzene sulfonate (NOBS) and tetraacetyl ethylene diamine (TAED) activators are typical, and mixtures thereof can also be used. See also U.S. 4,634,551 for other typical bleaches and activators useful herein.

Bleach Activators

10 Bleach activators useful herein include amides, imides, esters and anhydrides. Commonly at least one substituted or unsubstituted acyl moiety is present, covalently connected to a leaving group as in the structure $R-C(O)-L$. In one preferred mode of use, bleach activators are combined with a source of hydrogen peroxide, such as the perborates or percarbonates, in a single product. Conveniently, the single product leads
15 to in situ production in aqueous solution (i.e., during the washing process) of the percarboxylic acid corresponding to the bleach activator. The product itself can be hydrous, for example a powder, provided that water is controlled in amount and mobility such that storage stability is acceptable. Alternately, the product can be an anhydrous solid or liquid. In another mode, the bleach activator or oxygen bleach is
20 incorporated in a pretreatment product, such as a stain stick; soiled, pretreated substrates can then be exposed to further treatments, for example of a hydrogen peroxide source. With respect to the above bleach activator structure $RC(O)L$, the atom in the leaving group connecting to the peracid-forming acyl moiety $R(C)O-$ is most typically O or N. Bleach activators can have non-charged, positively or negatively charged peracid-
25 forming moieties and/or noncharged, positively or negatively charged leaving groups. One or more peracid-forming moieties or leaving-groups can be present. See, for example, U.S. 5,595,967, U.S. 5,561,235, U.S. 5,560,862 or the bis-(peroxy-carbonic) system of U.S. 5,534,179. Mixtures of suitable bleach activators can also be used. Bleach activators can be substituted with electron-donating or electron-releasing
30 moieties either in the leaving-group or in the peracid-forming moiety or moieties,

changing their reactivity and making them more or less suited to particular pH or wash conditions. For example, electron-withdrawing groups such as NO₂ improve the efficacy of bleach activators intended for use in mild-pH (e.g., from about 7.5- to about 9.5) wash conditions.

5 An extensive and exhaustive disclosure of suitable bleach activators and suitable leaving groups, as well as how to determine suitable activators, can be found in US Patents 5,686,014 and 5,622,646.

 Cationic bleach activators include quaternary carbamate-, quaternary carbonate-, quaternary ester- and quaternary amide- types, delivering a range of cationic
10 peroxyimidic, peroxy-carbonic or peroxy-carboxylic acids to the wash. An analogous but non-cationic palette of bleach activators is available when quaternary derivatives are not desired. In more detail, cationic activators include quaternary ammonium-substituted activators of WO 96-06915, U.S. 4,751,015 and 4,397,757, EP-A-284292, EP-A-331,229 and EP-A-03520. Also useful are cationic nitriles as disclosed in EP-A-
15 303,520 and in European Patent Specification 458,396 and 464,880. Other nitrile types have electron-withdrawing substituents as described in U.S. 5,591,378.

 Other bleach activator disclosures include GB 836,988; 864,798; 907,356; 1,003,310 and 1,519,351; German Patent 3,337,921; EP-A-0185522; EP-A-0174132; EP-A-0120591; U.S. Pat. Nos. 1,246,339; 3,332,882; 4,128,494; 4,412,934 and
20 4,675,393, and the phenol sulfonate ester of alkanoyl aminoacids disclosed in U.S. 5,523,434. Suitable bleach activators include any acetylated diamine types, whether hydrophilic or hydrophobic in character.

 Of the above classes of bleach precursors, preferred classes include the esters, including acyl phenol sulfonates, acyl alkyl phenol sulfonates or acyl
25 oxybenzenesulfonates (OBS leaving-group); the acyl-amides; and the quaternary ammonium substituted peroxyacid precursors including the cationic nitriles.

 Preferred bleach activators include N,N,N',N'-tetraacetyl ethylene diamine (TAED) or any of its close relatives including the triacetyl or other unsymmetrical derivatives. TAED and the acetylated carbohydrates such as glucose pentaacetate and tetraacetyl

xylose are preferred hydrophilic bleach activators. Depending on the application, acetyl triethyl citrate, a liquid, also has some utility, as does phenyl benzoate.

Preferred hydrophobic bleach activators include sodium nonanoyloxybenzene sulfonate (NOBS or SNOBS), N-(alkanoyl)aminoalkanoyloxy benzene sulfonates, such as
 5 4-[N-(nonanoyl)aminohexanoyloxy]-benzene sulfonate or (NACA-OBS) as described in US Patent 5,534,642 and in EPA 0 355 384 A1, substituted amide types described in detail hereinafter, such as activators related to NAPAA, and activators related to certain imidoperacid bleaches, for example as described in U.S. Patent 5,061,807, issued October 29, 1991 and assigned to Hoechst Aktiengesellschaft of Frankfurt, Germany and Japanese
 10 Laid-Open Patent Application (Kokai) No. 4-28799.

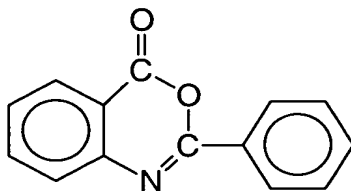
Another group of peracids and bleach activators herein are those derivable from acyclic imidoperoxydicarboxylic acids and salts thereof, See US Patent 5,415,796, and cyclic imidoperoxydicarboxylic acids and salts thereof, see US patents 5,061,807, 5,132,431, 5,654,269, 5,246,620, 5,419,864 and 5,438,147.

15 Other suitable bleach activators include sodium-4-benzoyloxy benzene sulfonate (SBOBS); sodium-1-methyl-2-benzoyloxy benzene-4-sulphonate; sodium-4-methyl-3-benzoyloxy benzoate (SPCC); trimethyl ammonium toluyloxy-benzene sulfonate; or sodium 3,5,5-trimethyl hexanoyloxybenzene sulfonate (STHOBS).

Bleach activators may be used in an amount of up to 20%, preferably from 0.1-
 20 10% by weight, of the composition, though higher levels, 40% or more, are acceptable, for example in highly concentrated bleach additive product forms or forms intended for appliance automated dosing.

Highly preferred bleach activators useful herein are amide-substituted and an extensive and exhaustive disclosure of these activators can be found in US Patents
 25 5,686,014 and 5,622,646.

Other useful activators, disclosed in U.S. 4,966,723, are benzoxazin-type, such as a C₆H₄ ring to which is fused in the 1,2-positions a moiety --C(O)OC(R¹)=N-. A highly preferred activator of the benzoxazin-type is:



Depending on the activator and precise application, good bleaching results can be obtained from bleaching systems having with in-use pH of from about 6 to about 13, preferably from about 9.0 to about 10.5. Typically, for example, activators with
5 electron-withdrawing moieties are used for near-neutral or sub-neutral pH ranges. Alkalis and buffering agents can be used to secure such pH.

Acyl lactam activators are very useful herein, especially the acyl caprolactams (see for example WO 94-28102 A) and acyl valerolactams (see U.S. 5,503,639). See also U.S. 4,545,784 which discloses acyl caprolactams, including benzoyl caprolactam
10 adsorbed into sodium perborate. In certain preferred embodiments of the invention, NOBS, lactam activators, imide activators or amide-functional activators, especially the more hydrophobic derivatives, are desirably combined with hydrophilic activators such as TAED, typically at weight ratios of hydrophobic activator : TAED in the range of 1:5 to 5:1, preferably about 1:1. Other suitable lactam activators are alpha-modified, see
15 WO 96-22350 A1, July 25, 1996. Lactam activators, especially the more hydrophobic types, are desirably used in combination with TAED, typically at weight ratios of amido-derived or caprolactam activators : TAED in the range of 1:5 to 5:1, preferably about 1:1. See also the bleach activators having cyclic amidine leaving-group disclosed in U.S. 5,552,556.

20 Nonlimiting examples of additional activators useful herein are to be found in U.S. 4,915,854, U.S. 4,412,934 and 4,634,551. The hydrophobic activator nonanoyloxybenzene sulfonate (NOBS) and the hydrophilic tetraacetyl ethylene diamine (TAED) activator are typical, and mixtures thereof can also be used.

Additional activators useful herein include those of U.S. 5,545,349, which is also
25 incorporated herein by reference.

Bleaches other than oxygen bleaching agents are also known in the art and can be utilized herein. One type of non-oxygen bleaching agent of particular interest includes

photoactivated bleaches such as the sulfonated zinc and/or aluminum phthalocyanines. See U.S. Patent 4,033,718, issued July 5, 1977 to Holcombe et al. If used, detergent compositions will typically contain from about 0.025% to about 1.25%, by weight, of such bleaches, especially sulfonate zinc phthalocyanine.

5 Bleach Catalysts

The present invention compositions and methods may optionally utilize metal-containing bleach catalysts that are effective for use in ADD, laundry or bleaching compositions. Preferred are manganese and cobalt-containing bleach catalysts.

For examples of suitable bleach catalysts see U.S. Pat. Nos. 4,246,612, 5,804,542, 10 5,798,326, 5,246,621, 4,430,243, 5,244,594, 5,597,936, 5,705,464, 4,810,410, 4,601,845, 5,194,416, 5,703,030, 4,728,455, 4,711,748, 4,626,373, 4,119,557, 5,114,606, 5,599,781, 5,703,034, 5,114,611, 4,430,243, 4,728,455, 5,720,897 and 5,227,084; EP Pat. Nos. 408,131, 549,271, 384,503, 549,272, 224,952, and 306,089; DE Pat. No. 2,054,019; CA Pat No. 866,191.

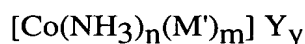
15 Preferred are cobalt (III) catalysts having the formula:



wherein cobalt is in the +3 oxidation state; n is an integer from 0 to 5 (preferably 4 or 5; most preferably 5); M' represents a monodentate ligand; m is an integer from 0 to 5 (preferably 1 or 2; most preferably 1); B' represents a bidentate ligand; b is an integer 20 from 0 to 2; T' represents a tridentate ligand; t is 0 or 1; Q is a tetradentate ligand; q is 0 or 1; P is a pentadentate ligand; p is 0 or 1; and $n + m + 2b + 3t + 4q + 5p = 6$; Y is one or more appropriately selected counteranions present in a number y, where y is an integer from 1 to 3 (preferably 2 to 3; most preferably 2 when Y is a -1 charged anion), to obtain a charge-balanced salt, preferred Y are selected from the group consisting of chloride, 25 iodide, I_3^- , formate, nitrate, nitrite, sulfate, sulfite, citrate, acetate, carbonate, bromide, PF_6^- , BF_4^- , $\text{B}(\text{Ph})_4^-$, phosphate, phosphite, silicate, tosylate, methanesulfonate, and combinations thereof [optionally, Y can be protonated if more than one anionic group exists in Y, e.g., HPO_4^{2-} , HCO_3^- , H_2PO_4^- , etc., and further, Y may be selected from the group consisting of non-traditional inorganic anions such as anionic surfactants, e.g.,

linear alkylbenzene sulfonates (LAS), alkyl sulfates (AS), alkylethoxysulfonates (AES), etc., and/or anionic polymers, e.g., polyacrylates, polymethacrylates, etc.]; and wherein further at least one of the coordination sites attached to the cobalt is labile under automatic dishwashing use conditions and the remaining coordination sites stabilize the cobalt under automatic dishwashing conditions such that the reduction potential for cobalt (III) to cobalt (II) under alkaline conditions is less than about 0.4 volts (preferably less than about 0.2 volts) versus a normal hydrogen electrode.

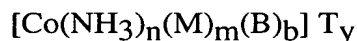
Preferred cobalt catalysts of this type have the formula:



wherein n is an integer from 3 to 5 (preferably 4 or 5; most preferably 5); M' is a labile coordinating moiety, preferably selected from the group consisting of chlorine, bromine, hydroxide, water, and (when m is greater than 1) combinations thereof; m is an integer from 1 to 3 (preferably 1 or 2; most preferably 1); m+n = 6; and Y is an appropriately selected counteranion present in a number y, which is an integer from 1 to 3 (preferably 2 to 3; most preferably 2 when Y is a -1 charged anion), to obtain a charge-balanced salt.

The preferred cobalt catalyst of this type useful herein are cobalt pentaamine chloride salts having the formula $[\text{Co}(\text{NH}_3)_5\text{Cl}] \text{Y}_y$, and especially $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$.

More preferred are the present invention compositions which utilize cobalt (III) bleach catalysts having the formula:



wherein cobalt is in the +3 oxidation state; n is 4 or 5 (preferably 5); M is one or more ligands coordinated to the cobalt by one site; m is 0, 1 or 2 (preferably 1); B is a ligand coordinated to the cobalt by two sites; b is 0 or 1 (preferably 0), and when b=0, then m+n = 6, and when b=1, then m=0 and n=4; and T is one or more appropriately selected counteranions present in a number y, where y is an integer to obtain a charge-balanced salt (preferably y is 1 to 3; most preferably 2 when T is a -1 charged anion); and wherein further said catalyst has a base hydrolysis rate constant of less than $0.23 \text{ M}^{-1} \text{ s}^{-1}$ (25°C).

The most preferred cobalt catalyst useful herein are cobalt pentaamine acetate salts having the formula $[\text{Co}(\text{NH}_3)_5\text{OAc}] \text{ T}_y$, wherein OAc represents an acetate moiety, and especially cobalt pentaamine acetate chloride, $[\text{Co}(\text{NH}_3)_5\text{OAc}]\text{Cl}_2$; as well as $[\text{Co}(\text{NH}_3)_5\text{OAc}](\text{OAc})_2$; $[\text{Co}(\text{NH}_3)_5\text{OAc}](\text{PF}_6)_2$; $[\text{Co}(\text{NH}_3)_5\text{OAc}](\text{SO}_4)$; $[\text{Co}(\text{NH}_3)_5\text{OAc}](\text{BF}_4)_2$; and $[\text{Co}(\text{NH}_3)_5\text{OAc}](\text{NO}_3)_2$.

As a practical matter, and not by way of limitation, the cleaning compositions and cleaning processes herein can be adjusted to provide on the order of at least one part per hundred million of the active bleach catalyst species, when present, in the aqueous washing medium, and will more preferably provide from about 0.01 ppm to about 25 ppm, more preferably from about 0.05 ppm to about 10 ppm, and most preferably from about 0.1 ppm to about 5 ppm, of the bleach catalyst species in the wash liquor. In order to obtain such levels in the wash liquor of an automatic dishwashing process, typical automatic dishwashing compositions herein will comprise from about 0.0005% to about 0.2%, more preferably from about 0.004% to about 0.08%, of bleach catalyst by weight of the cleaning compositions.

Builders - Builders can operate via a variety of mechanisms including forming soluble or insoluble complexes with hardness ions, by ion exchange, and by offering a surface more favorable to the precipitation of hardness ions than are the surfaces of articles to be cleaned. Builder level can vary widely depending upon end use and physical form of the composition. For example, high-surfactant formulations can be unbuilt. The level of builder can vary widely depending upon the end use of the composition and its desired physical form. The compositions will comprise at least about 0.1%, preferably from about 1% to about 90%, more preferably from about 5% to about 80%, even more preferably from about 10% to about 40% by weight, of the detergent builder. Lower or higher levels of builder, however, are not excluded.

Suitable builders herein can be selected from the group consisting of phosphates and polyphosphates, especially the sodium salts; carbonates, bicarbonates, sesquicarbonates and carbonate minerals other than sodium carbonate or sesquicarbonate; organic mono-, di-, tri-, and tetracarboxylates especially water-soluble nonsurfactant carboxylates in acid, sodium, potassium or alkanolammonium salt form, as well as

oligomeric or water-soluble low molecular weight polymer carboxylates including aliphatic and aromatic types; and phytic acid. These may be complemented by borates, e.g., for pH-buffering purposes, or by sulfates, especially sodium sulfate and any other fillers or carriers which may be important to the engineering of stable surfactant and/or
5 builder-containing detergent compositions.

Builder mixtures, sometimes termed "builder systems" can be used and typically comprise two or more conventional builders, optionally complemented by chelants, pH-buffers or fillers, though these latter materials are generally accounted for separately when describing quantities of materials herein. In terms of relative quantities of surfactant and
10 builder in the present granular compositions, preferred builder systems are typically formulated at a weight ratio of surfactant to builder of from about 60:1 to about 1:80. Certain preferred granular detergents have said ratio in the range 0.90:1.0 to 4.0:1.0, more preferably from 0.95:1.0 to 3.0:1.0.

P-containing detergent builders often preferred where permitted by legislation
15 include, but are not limited to, the alkali metal, ammonium and alkanolammonium salts of polyphosphates exemplified by the tripolyphosphates, pyrophosphates, glassy polymeric meta-phosphates; and phosphonates. Where phosphorus-based builders can be used, the various alkali metal phosphates such as the well-known sodium tripolyphosphates, sodium pyrophosphate and sodium orthophosphate can be used. Phosphonate builders
20 such as ethane-1-hydroxy-1,1-diphosphonate and other known phosphonates (see, for example, U.S. Patents 3,159,581; 3,213,030; 3,422,021; 3,400,148 and 3,422,137) can also be used though such materials are more commonly used in a low-level mode as chelants or stabilizers.

Phosphate detergent builders for use in granular compositions are well known.
25 They include, but are not limited to, the alkali metal, ammonium and alkanolammonium salts of polyphosphates (exemplified by the tripolyphosphates, pyrophosphates, and glassy polymeric meta-phosphates). Phosphate builder sources are described in detail in Kirk Othmer, 3rd Edition, Vol. 17, pp. 426-472 and in "Advanced Inorganic Chemistry" by Cotton and Wilkinson, pp. 394-400 (John Wiley and Sons, Inc.; 1972).

Preferred levels of phosphate builders herein are from about 10% to about 75%, preferably from about 15% to about 50%, of phosphate builder.

Phosphate builders can optionally be included in the compositions herein to assist in controlling mineral hardness. Builders are typically used in automatic dishwashing to assist in the removal of particulate soils.

Suitable carbonate builders include alkaline earth and alkali metal carbonates as disclosed in German Patent Application No. 2,321,001 published on November 15, 1973, although sodium bicarbonate, sodium carbonate, sodium sesquicarbonate, and other carbonate minerals such as trona or any convenient multiple salts of sodium carbonate and calcium carbonate such as those having the composition $2\text{Na}_2\text{CO}_3 \cdot \text{CaCO}_3$ when anhydrous, and even calcium carbonates including calcite, aragonite and vaterite, especially forms having high surface areas relative to compact calcite may be useful, for example as seeds. Various grades and types of sodium carbonate and sodium sesquicarbonate may be used, certain of which are particularly useful as carriers for other ingredients, especially deterative surfactants.

Suitable organic detergent builders include polycarboxylate compounds, including water-soluble nonsurfactant dicarboxylates and tricarboxylates. More typically builder polycarboxylates have a plurality of carboxylate groups, preferably at least 3 carboxylates. Carboxylate builders can be formulated in acid, partially neutral, neutral or overbased form. When in salt form, alkali metals, such as sodium, potassium, and lithium, or alkanolammonium salts are preferred. Polycarboxylate builders include the ether polycarboxylates, such as oxydisuccinate, see Berg, U.S. 3,128,287, April 7, 1964, and Lamberti et al, U.S. 3,635,830, January 18, 1972; "TMS/TDS" builders of U.S. 4,663,071, Bush et al, May 5, 1987; and other ether carboxylates including cyclic and alicyclic compounds, such as those described in U.S. Patents 3,923,679; 3,835,163; 4,158,635; 4,120,874 and 4,102,903.

Other suitable builders are the ether hydroxypolycarboxylates, copolymers of maleic anhydride with ethylene or vinyl methyl ether; 1, 3, 5-trihydroxy benzene-2, 4, 6-trisulphonic acid; carboxymethyloxysuccinic acid; the various alkali metal, ammonium and substituted ammonium salts of polyacetic acids such as ethylenediamine tetraacetic

acid and nitrilotriacetic acid; as well as mellitic acid, succinic acid, oxydisuccinic acid, polymaleic acid, benzene 1,3,5-tricarboxylic acid, carboxymethyloxysuccinic acid, and soluble salts thereof.

Citrates, e.g., citric acid and soluble salts thereof are important carboxylate builders due to availability from renewable resources and biodegradability. Citrates can also be used in the present granular compositions, especially in combination with zeolite and/or layered silicates. Citrates can also be used in combination with zeolite, the hereafter mentioned BRITESIL types, and/or layered silicate builders. Oxydisuccinates are also useful in such compositions and combinations. Oxydisuccinates are also especially useful in such compositions and combinations.

Where permitted alkali metal phosphates such as sodium tripolyphosphates, sodium pyrophosphate and sodium orthophosphate can be used. Phosphonate builders such as ethane-1-hydroxy-1,1-diphosphonate and other known phosphonates, e.g., those of U.S. 3,159,581; 3,213,030; 3,422,021; 3,400,148 and 3,422,137 can also be used and may have desirable antiscaling properties.

Certain deterative surfactants or their short-chain homologs also have a builder action. For unambiguous formula accounting purposes, when they have surfactant capability, these materials are summed up as deterative surfactants. Preferred types for builder functionality are illustrated by: 3,3-dicarboxy-4-oxa-1,6-hexanedioates and the related compounds disclosed in U.S. 4,566,984, Bush, January 28, 1986. Succinic acid builders include the C₅-C₂₀ alkyl and alkenyl succinic acids and salts thereof. Succinate builders also include: laurylsuccinate, myristylsuccinate, palmitylsuccinate, 2-dodecenylsuccinate (preferred), 2-pentadecenylsuccinate, and the like. Lauryl-succinates are described in European Patent Application 86200690.5/0,200,263, published November 5, 1986. Fatty acids, e.g., C₁₂-C₁₈ monocarboxylic acids, can also be incorporated into the compositions as surfactant/builder materials alone or in combination with the aforementioned builders, especially citrate and/or the succinate builders, to provide additional builder activity but are generally not desired. Such use of fatty acids will generally result in a diminution of sudsing in laundry compositions, which may need to be taken into account by the formulator. Fatty acids or their salts are undesirable in

Automatic Dishwashing (ADD) embodiments in situations wherein soap scums can form and be deposited on dishware. . Other suitable polycarboxylates are disclosed in U.S. 4,144,226, Crutchfield et al, March 13, 1979 and in U.S. 3,308,067, Diehl, March 7, 1967. See also Diehl, U.S. 3,723,322.

- 5 Other types of inorganic builder materials which can be used have the formula $(M_x)_i Ca_y (CO_3)_z$ wherein x and i are integers from 1 to 15, y is an integer from 1 to 10, z is an integer from 2 to 25, M_i are cations, at least one of which is a water-soluble, and the equation $\sum_{i=1-15} (x_i \text{ multiplied by the valence of } M_i) + 2y = 2z$ is satisfied such that the formula has a neutral or "balanced" charge. These builders are referred to herein as
- 10 "Mineral Builders". Waters of hydration or anions other than carbonate may be added provided that the overall charge is balanced or neutral. The charge or valence effects of such anions should be added to the right side of the above equation. Preferably, there is present a water-soluble cation selected from the group consisting of hydrogen, water-soluble metals, hydrogen, boron, ammonium, silicon, and mixtures thereof, more
- 15 preferably, sodium, potassium, hydrogen, lithium, ammonium and mixtures thereof, sodium and potassium being highly preferred. Nonlimiting examples of noncarbonate anions include those selected from the group consisting of chloride, sulfate, fluoride, oxygen, hydroxide, silicon dioxide, chromate, nitrate, borate and mixtures thereof. Preferred builders of this type in their simplest forms are selected from the group
- 20 consisting of $Na_2Ca(CO_3)_2$, $K_2Ca(CO_3)_2$, $Na_2Ca_2(CO_3)_3$, $NaKCa(CO_3)_2$, $NaKCa_2(CO_3)_3$, $K_2Ca_2(CO_3)_3$, and combinations thereof. An especially preferred material for the builder described herein is $Na_2Ca(CO_3)_2$ in any of its crystalline modifications. Suitable builders of the above-defined type are further illustrated by, and include, the natural or synthetic forms of any one or combinations of the following
- 25 minerals: Afghanite, Andersonite, AshcroftineY, Beyerite, Borcarite, Burbankite, Butschliite, Cancrinite, Carbocernaite, Carletonite, Davyne, DonnayiteY, Fairchildite, Ferrisurite, Franzinite, Gaudefroyite, Gaylussite, Girvasite, Gregoryite, Jouravskite, KamphaugiteY, Kettnerite, Khanneshite, LepersonniteGd, Liottite, MckelveyiteY, Microsommite, Mroseite, Natrofairchildite, Nyerereite, RemonditeCe, Sacrofanite,

Schrockingerite, Shortite, Surite, Tunisite, Tuscanite, Tyrolite, Vishnevite, and Zemkorite. Preferred mineral forms include Nyererite, Fairchildite and Shortite.

Detergent builders can also be selected from aluminosilicates and silicates, for example to assist in controlling mineral, especially Ca and/or Mg, hardness in wash water
5 or to assist in the removal of particulate soils from surfaces.

Suitable silicate builders include water-soluble and hydrous solid types and including those having chain-, layer-, or three-dimensional- structure as well as amorphous-solid or non-structured-liquid types. Preferred are alkali metal silicates, particularly those liquids and solids having a $\text{SiO}_2\text{:Na}_2\text{O}$ ratio in the range 1.6:1 to 3.2:1,
10 including, particularly for automatic dishwashing purposes, solid hydrous 2-ratio silicates marketed by PQ Corp. under the tradename BRITESIL[®], e.g., BRITESIL H₂O; and layered silicates, e.g., those described in U.S. 4,664,839, May 12, 1987, H. P. Rieck. NaSKS-6, sometimes abbreviated "SKS-6", is a crystalline layered aluminium-free δ - Na_2SiO_5 morphology silicate marketed by Hoechst and is preferred especially in granular
15 laundry compositions. See preparative methods in German DE-A-3,417,649 and DE-A-3,742,043. Other layered silicates, such as those having the general formula $\text{NaMSi}_x\text{O}_{2x+1}\cdot y\text{H}_2\text{O}$ wherein M is sodium or hydrogen, x is a number from 1.9 to 4, preferably 2, and y is a number from 0 to 20, preferably 0, can also or alternately be used herein. Layered silicates from Hoechst also include NaSKS-5, NaSKS-7 and NaSKS-11,
20 as the α , β and γ layer-silicate forms. Other silicates may also be useful, such as magnesium silicate, which can serve as a crispening agent in granules, as a stabilising agent for bleaches, and as a component of suds control systems.

Also suitable for use herein are synthesized crystalline ion exchange materials or hydrates thereof having chain structure and a composition represented by the following
25 general formula in an anhydride form: $x\text{M}_2\text{O}\cdot y\text{SiO}_2\cdot z\text{M}'\text{O}$ wherein M is Na and/or K, M' is Ca and/or Mg; y/x is 0.5 to 2.0 and z/x is 0.005 to 1.0 as taught in U.S. 5,427,711, Sakaguchi et al, June 27, 1995.

Aluminosilicate builders are especially useful in granular compositions, but can also be incorporated in liquids, pastes or gels. Suitable for the present purposes are those

having empirical formula: $[M_z(AlO_2)_z(SiO_2)_v] \cdot xH_2O$ wherein z and v are integers of at least 6, the molar ratio of z to v is in the range from 1.0 to 0.5, and x is an integer from 15 to 264. Aluminosilicates can be crystalline or amorphous, naturally-occurring or synthetically derived. An aluminosilicate production method is in U.S. 3,985,669, Krummel, et al, October 12, 1976. Preferred synthetic crystalline aluminosilicate ion exchange materials are available as Zeolite A, Zeolite P (B), Zeolite X and, to whatever extent this differs from Zeolite P, the so-called Zeolite MAP. Natural types, including clinoptilolite, may be used. Zeolite A has the formula: $Na_{12}[(AlO_2)_{12}(SiO_2)_{12}] \cdot xH_2O$ wherein x is from 20 to 30, especially 27. Dehydrated zeolites ($x = 0 - 10$) may also be used. Preferably, the aluminosilicate has a particle size of 0.1-10 microns in diameter.

Detergent builders other than silicates can be used in the compositions herein to assist in controlling mineral hardness. They can be used in conjunction with or instead of aluminosilicates and silicates. Inorganic as well as organic builders can be used. Builders are used in automatic dishwashing to assist in the removal of particulate soils.

Inorganic or non-phosphate-containing detergent builders include, but are not limited to, phosphonates, phytic acid, carbonates (including bicarbonates and sesquicarbonates), sulfates, citrate, zeolite, and aluminosilicates.

Aluminosilicate builders may be used in the present compositions though are not preferred for automatic dishwashing detergents. (See U.S. Pat. 4,605,509 for examples of preferred aluminosilicates.) Aluminosilicate builders are of great importance in most currently marketed heavy duty granular detergent compositions, and can also be a significant builder ingredient in liquid detergent formulations. Aluminosilicate builders include those having the empirical formula: $Na_2O \cdot Al_2O_3 \cdot xSiO_2 \cdot yH_2O$ wherein z and y are integers of at least 6, the molar ratio of z to y is in the range from 1.0 to about 0.5, and x is an integer from about 15 to about 264.

Useful aluminosilicate ion exchange materials are commercially available. These aluminosilicates can be crystalline or amorphous in structure and can be naturally-occurring aluminosilicates or synthetically derived. A method for producing aluminosilicate ion exchange materials is disclosed in U.S. Patent 3,985,669, Krummel, et

al, issued October 12, 1976. Preferred synthetic crystalline aluminosilicate ion exchange materials useful herein are available under the designations Zeolite A, Zeolite P (B), Zeolite MAP and Zeolite X. In another embodiment, the crystalline aluminosilicate ion exchange material has the formula: $\text{Na}_{12}[(\text{AlO}_2)_{12}(\text{SiO}_2)_{12}] \cdot x\text{H}_2\text{O}$ wherein x is from about 20 to about 30, especially about 27. This material is known as Zeolite A. Dehydrated zeolites ($x = 0 - 10$) may also be used herein. Preferably, the aluminosilicate has a particle size of about 0.1-10 microns in diameter. Individual particles can desirably be even smaller than 0.1 micron to further assist kinetics of exchange through maximization of surface area. High surface area also increases utility of aluminosilicates as adsorbents for surfactants, especially in granular compositions. Aggregates of aluminosilicate particles may be useful, a single aggregate having dimensions tailored to minimize segregation in granular compositions, while the aggregate particle remains dispersible to submicron individual particles during the wash. As with other builders such as carbonates, it may be desirable to use zeolites in any physical or morphological form adapted to promote surfactant carrier function, and appropriate particle sizes may be freely selected by the formulator.

Polymeric Soil Release Agent - The compositions according to the present invention may optionally comprise one or more soil release agents. Polymeric soil release agents are characterized by having both hydrophilic segments, to hydrophilize the surface of hydrophobic fibers, such as polyester and nylon, and hydrophobic segments, to deposit upon hydrophobic fibers and remain adhered thereto through completion of the laundry cycle and , thus, serve as an anchor for the hydrophilic segments. This can enable stains occurring subsequent to treatment with the soil release agent to be more easily cleaned in later washing procedures.

If utilized, soil release agents will generally comprise from about 0.01% to about 10% preferably from about 0.1% to about 5%, more preferably from about 0.2% to about 3% by weight, of the composition.

The following, all included herein by reference, describe soil release polymers suitable for use in the present invention. U.S. 5,691,298 Gosselink et al., issued November 25, 1997; U.S. 5,599,782 Pan et al., issued February 4, 1997; U.S. 5,415,807 Gosselink et

al., issued May 16, 1995; U.S. 5,182,043 Morrall et al., issued January 26, 1993; U.S. 4,956,447 Gosselink et al., issued September 11, 1990; U.S. 4,976,879 Maldonado et al. issued December 11, 1990; U.S. 4,968,451 Scheibel et al., issued November 6, 1990; U.S. 4,925,577 Borchert, Sr. et al., issued May 15, 1990; U.S. 4,861,512 Gosselink, issued
5 August 29, 1989; U.S. 4,877,896 Maldonado et al., issued October 31, 1989; U.S. 4,702,857 Gosselink et al., issued October 27, 1987; U.S. 4,711,730 Gosselink et al., issued December 8, 1987; U.S. 4,721,580 Gosselink issued January 26, 1988; U.S. 4,000,093 Nicol et al., issued December 28, 1976; U.S. 3,959,230 Hayes, issued May 25, 1976; U.S. 3,893,929 Basadur, issued July 8, 1975; and European Patent Application 0
10 219 048, published April 22, 1987 by Kud et al.

Further suitable soil release agents are described in U.S. 4,201,824 Voilland et al.; U.S. 4,240,918 Lagasse et al.; U.S. 4,525,524 Tung et al.; U.S. 4,579,681 Ruppert et al.; U.S. 4,220,918; U.S. 4,787,989; EP 279,134 A, 1988 to Rhone-Poulenc Chemie; EP 457,205 A to BASF (1991); and DE 2,335,044 to Unilever N.V., 1974; all incorporated
15 herein by reference.

Clay Soil Removal/Anti-redeposition Agents - The compositions of the present invention can also optionally contain water-soluble ethoxylated amines having clay soil removal and antiredeposition properties. Granular compositions which contain these compounds typically contain from about 0.01% to about 10.0% by weight of the water-
20 soluble ethoxylates amines; liquid detergent compositions typically contain about 0.01% to about 5%.

Polymeric Dispersing Agents - Polymeric dispersing agents can advantageously be utilized at levels from about 0.1% to about 7%, by weight, in the compositions herein, especially in the presence of zeolite and/or layered silicate builders. Suitable polymeric
25 dispersing agents include polymeric polycarboxylates and polyethylene glycols, although others known in the art can also be used. It is believed, though it is not intended to be limited by theory, that polymeric dispersing agents enhance overall detergent builder performance, when used in combination with other builders (including lower molecular weight polycarboxylates) by crystal growth inhibition, particulate soil release peptization,
30 and anti-redeposition.

Polymeric polycarboxylate materials can be prepared by polymerizing or copolymerizing suitable unsaturated monomers, preferably in their acid form. Unsaturated monomeric acids that can be polymerized to form suitable polymeric polycarboxylates include acrylic acid, maleic acid (or maleic anhydride), fumaric acid, itaconic acid, aconitic acid, mesaconic acid, citraconic acid and methylenemalononic acid. The presence in the polymeric polycarboxylates herein or monomeric segments, containing no carboxylate radicals such as vinylmethyl ether, styrene, ethylene, etc. is suitable provided that such segments do not constitute more than about 40% by weight.

Particularly suitable polymeric polycarboxylates can be derived from acrylic acid. Such acrylic acid-based polymers which are useful herein are the water-soluble salts of polymerized acrylic acid. The average molecular weight of such polymers in the acid form preferably ranges from about 2,000 to 10,000, more preferably from about 4,000 to 7,000 and most preferably from about 4,000 to 5,000. Water-soluble salts of such acrylic acid polymers can include, for example, the alkali metal, ammonium and substituted ammonium salts. Soluble polymers of this type are known materials. Use of polyacrylates of this type in detergent compositions has been disclosed, for example, in Diehl, U.S. Patent 3,308,067, issued march 7, 1967.

Acrylic/maleic-based copolymers may also be used as a preferred component of the dispersing/anti-redeposition agent. Such materials include the water-soluble salts of copolymers of acrylic acid and maleic acid. The average molecular weight of such copolymers in the acid form preferably ranges from about 2,000 to 100,000, more preferably from about 5,000 to 75,000, most preferably from about 7,000 to 65,000. The ratio of acrylate to maleate segments in such copolymers will generally range from about 30:1 to about 1:1, more preferably from about 10:1 to 2:1. Water-soluble salts of such acrylic acid/maleic acid copolymers can include, for example, the alkali metal, ammonium and substituted ammonium salts. Soluble acrylate/maleate copolymers of this type are known materials which are described in European Patent Application No. 66915, published December 15, 1982, as well as in EP 193,360, published September 3, 1986, which also describes such polymers comprising hydroxypropylacrylate. Still other useful dispersing agents include the maleic/acrylic/vinyl alcohol terpolymers. Such materials are

also disclosed in EP 193,360, including, for example, the 45/45/10 terpolymer of acrylic/maleic/vinyl alcohol.

Another polymeric material which can be included is polyethylene glycol (PEG). PEG can exhibit dispersing agent performance as well as act as a clay soil removal-
5 antiredeposition agent. Typical molecular weight ranges for these purposes range from about 500 to about 100,000, preferably from about 1,000 to about 50,000, more preferably from about 1,500 to about 10,000.

Polyaspartate and polyglutamate dispersing agents may also be used, especially in conjunction with zeolite builders. Dispersing agents such as polyaspartate preferably
10 have a molecular weight (avg.) of about 10,000.

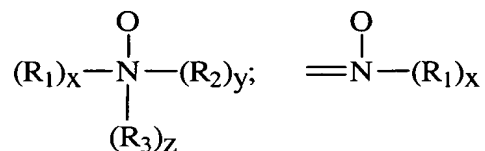
Brightener - Any optical brighteners or other brightening or whitening agents known in the art can be incorporated at levels typically from about 0.01% to about 1.2%, by weight, into the detergent compositions herein. Commercial optical brighteners which may be useful in the present invention can be classified into subgroups, which include,
15 but are not necessarily limited to, derivatives of stilbene, pyrazoline, coumarin, carboxylic acid, methinecyanines, dibenzothiophene-5,5-dioxide, azoles, 5- and 6-membered-ring heterocycles, and other miscellaneous agents. Examples of such brighteners are disclosed in "The Production and Application of Fluorescent Brightening Agents", M. Zahradnik, Published by John Wiley & Sons, New York (1982).

20 Specific examples of optical brighteners which are useful in the present compositions are those identified in U.S. Patent 4,790,856, issued to Wixon on December 13, 1988. These brighteners include the PHORWHITE series of brighteners from Verona. Other brighteners disclosed in this reference include: Tinopal UNPA, Tinopal CBS and Tinopal 5BM; available from Ciba-Geigy; Artic White CC and Artic White CWD, the 2-
25 (4-styryl-phenyl)-2H-naphtho[1,2-d]triazoles; 4,4'-bis-(1,2,3-triazol-2-yl)-stilbenes; 4,4'-bis(styryl)bisphenyls; and the aminocoumarins. Specific examples of these brighteners include 4-methyl-7-diethyl- amino coumarin; 1,2-bis(benzimidazol-2-yl)ethylene; 1,3-diphenyl-pyrazolines; 2,5-bis(benzoxazol-2-yl)thiophene; 2-styryl-naphtho[1,2-d]oxazole; and 2-(stilben-4-yl)-2H-naphtho[1,2-d]triazole. See also U.S. Patent 3,646,015, issued
30 February 29, 1972 to Hamilton.

Dye Transfer Inhibiting Agents - The compositions of the present invention may also include one or more materials effective for inhibiting the transfer of dyes from one fabric to another during the cleaning process. Generally, such dye transfer inhibiting agents include polyvinyl pyrrolidone polymers, polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, manganese phthalocyanine, peroxidases, and mixtures thereof. If used, these agents typically comprise from about 0.01% to about 10% by weight of the composition, preferably from about 0.01% to about 5%, and more preferably from about 0.05% to about 2%.

More specifically, the polyamine N-oxide polymers preferred for use herein contain units having the following structural formula: $R-A_x-P$; wherein P is a polymerizable unit to which an N-O group can be attached or the N-O group can form part of the polymerizable unit or the N-O group can be attached to both units; A is one of the following structures: $-NC(O)-$, $-C(O)O-$, $-S-$, $-O-$, $-N=$; x is 0 or 1; and R is aliphatic, ethoxylated aliphatics, aromatics, heterocyclic or alicyclic groups or any combination thereof to which the nitrogen of the N-O group can be attached or the N-O group is part of these groups. Preferred polyamine N-oxides are those wherein R is a heterocyclic group such as pyridine, pyrrole, imidazole, pyrrolidine, piperidine and derivatives thereof.

The N-O group can be represented by the following general structures:



wherein R_1 , R_2 , R_3 are aliphatic, aromatic, heterocyclic or alicyclic groups or combinations thereof; x, y and z are 0 or 1; and the nitrogen of the N-O group can be attached or form part of any of the aforementioned groups. The amine oxide unit of the polyamine N-oxides has a $pK_a < 10$, preferably $pK_a < 7$, more preferred $pK_a < 6$.

Any polymer backbone can be used as long as the amine oxide polymer formed is water-soluble and has dye transfer inhibiting properties. Examples of suitable polymeric backbones are polyvinyls, polyalkylenes, polyesters, polyethers, polyamide, polyimides, polyacrylates and mixtures thereof. These polymers include random or block copolymers

where one monomer type is an amine N-oxide and the other monomer type is an N-oxide. The amine N-oxide polymers typically have a ratio of amine to the amine N-oxide of 10:1 to 1:1,000,000. However, the number of amine oxide groups present in the polyamine oxide polymer can be varied by appropriate copolymerization or by an appropriate degree of N-oxidation. The polyamine oxides can be obtained in almost any degree of polymerization. Typically, the average molecular weight is within the range of 500 to 1,000,000; more preferred 1,000 to 500,000; most preferred 5,000 to 100,000. This preferred class of materials can be referred to as "PVNO".

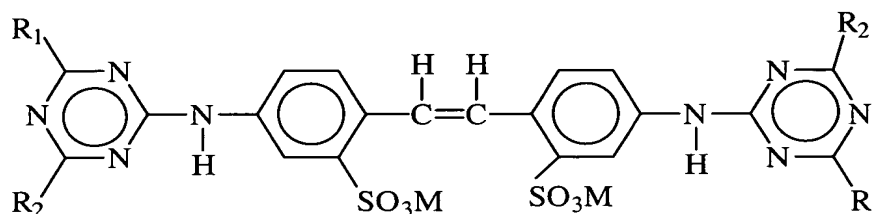
The most preferred polyamine N-oxide useful in the detergent compositions herein is poly(4-vinylpyridine-N-oxide) which as an average molecular weight of about 50,000 and an amine to amine N-oxide ratio of about 1:4.

Copolymers of N-vinylpyrrolidone and N-vinylimidazole polymers (referred to as a class as "PVPVI") are also preferred for use herein. Preferably the PVPVI has an average molecular weight range from 5,000 to 1,000,000, more preferably from 5,000 to 200,000, and most preferably from 10,000 to 20,000. (The average molecular weight range is determined by light scattering as described in Barth, et al., Chemical Analysis, Vol 113. "Modern Methods of Polymer Characterization", the disclosures of which are incorporated herein by reference.) The PVPVI copolymers typically have a molar ratio of N-vinylimidazole to N-vinylpyrrolidone from 1:1 to 0.2:1, more preferably from 0.8:1 to 0.3:1, most preferably from 0.6:1 to 0.4:1. These copolymers can be either linear or branched.

The present invention compositions also may employ a polyvinylpyrrolidone ("PVP") having an average molecular weight of from about 5,000 to about 400,000, preferably from about 5,000 to about 200,000, and more preferably from about 5,000 to about 50,000. PVP's are known to persons skilled in the detergent field; see, for example, EP-A-262,897 and EP-A-256,696, incorporated herein by reference. Compositions containing PVP can also contain polyethylene glycol ("PEG") having an average molecular weight from about 500 to about 100,000, preferably from about 1,000 to about 10,000. Preferably, the ratio of PEG to PVP on a ppm basis delivered in wash solutions is from about 2:1 to about 50:1, and more preferably from about 3:1 to about 10:1.

The compositions herein may also optionally contain from about 0.005% to 5% by weight of certain types of hydrophilic optical brighteners which also provide a dye transfer inhibition action. If used, the compositions herein will preferably comprise from about 0.01% to 1% by weight of such optical brighteners.

- 5 The hydrophilic optical brighteners useful in the present invention are those having the structural formula:



- wherein R_1 is selected from anilino, N-2-bis-hydroxyethyl and NH-2-hydroxyethyl; R_2 is selected from N-2-bis-hydroxyethyl, N-2-hydroxyethyl-N-methylamino, morphilino, chloro and amino; and M is a salt-forming cation such as sodium or potassium.
- 10

- When in the above formula, R_1 is anilino, R_2 is N-2-bis-hydroxyethyl and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-(N-2-bis-hydroxyethyl)-s-triazine-2-yl)amino]-2,2'-stilbenedisulfonic acid and disodium salt. This particular brightener species is commercially marketed under the tradename Tinopal-UNPA-GX by Ciba-Geigy Corporation. Tinopal-UNPA-GX is the preferred hydrophilic optical brightener useful in the detergent compositions herein.
- 15

- When in the above formula, R_1 is anilino, R_2 is N-2-hydroxyethyl-N-2-methylamino and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-(N-2-hydroxyethyl-N-methylamino)-s-triazine-2-yl)amino]-2,2'-stilbenedisulfonic acid disodium salt. This particular brightener species is commercially marketed under the tradename Tinopal 5BM-GX by Ciba-Geigy Corporation.
- 20

- When in the above formula, R_1 is anilino, R_2 is morphilino and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-morphilino-s-triazine-2-yl)amino]-2,2'-stilbenedisulfonic acid, sodium salt. This particular brightener species is commercially marketed under the tradename Tinopal AMS-GX by Ciba Geigy Corporation.
- 25

The specific optical brightener species selected for use in the present invention provide especially effective dye transfer inhibition performance benefits when used in combination with the selected polymeric dye transfer inhibiting agents hereinbefore described. The combination of such selected polymeric materials (e.g., PVNO and/or PVPVI) with such selected optical brighteners (e.g., Tinopal UNPA-GX, Tinopal 5BM-GX and/or Tinopal AMS-GX) provides significantly better dye transfer inhibition in aqueous wash solutions than does either of these two granular composition components when used alone. Without being bound by theory, it is believed that such brighteners work this way because they have high affinity for fabrics in the wash solution and therefore deposit relatively quick on these fabrics. The extent to which brighteners deposit on fabrics in the wash solution can be defined by a parameter called the "exhaustion coefficient". The exhaustion coefficient is in general as the ratio of a) the brightener material deposited on fabric to b) the initial brightener concentration in the wash liquor. Brighteners with relatively high exhaustion coefficients are the most suitable for inhibiting dye transfer in the context of the present invention.

Of course, it will be appreciated that other, conventional optical brightener types of compounds can optionally be used in the present compositions to provide conventional fabric "brightness" benefits, rather than a true dye transfer inhibiting effect. Such usage is conventional and well-known to detergent formulations.


Suds Suppressors - Compounds for reducing or suppressing the formation of suds can be incorporated into the compositions of the present invention. Suds suppression can be of particular importance in the so-called "high concentration cleaning process" as described in U.S. 4,489,455 and 4,489,574 and in front-loading European-style washing machines.

A wide variety of materials may be used as suds suppressors, and suds suppressors are well known to those skilled in the art. See, for example, Kirk Othmer Encyclopedia of Chemical Technology, Third Edition, Volume 7, pages 430-447 (John Wiley & Sons, Inc., 1979). One category of suds suppressor of particular interest encompasses monocarboxylic fatty acid and soluble salts therein. See U.S. Patent 2,954,347, issued September 27, 1960 to Wayne St. John. The monocarboxylic fatty acids and salts thereof

used as suds suppressor typically have hydrocarbyl chains of 10 to about 24 carbon atoms, preferably 12 to 18 carbon atoms. Suitable salts include the alkali metal salts such as sodium, potassium, and lithium salts, and ammonium and alkanolammonium salts.

The compositions herein may also contain non-surfactant suds suppressors. These
5 include, for example: high molecular weight hydrocarbons such as paraffin, fatty acid esters (e.g., fatty acid triglycerides), fatty acid esters of monovalent alcohols, aliphatic C₁₈-C₄₀ ketones (e.g., stearone), etc. Other suds inhibitors include N-alkylated amino triazines such as tri- to hexa-alkylmelamines or di- to tetra-alkyldiamine chlortriazines formed as products of cyanuric chloride with two or three moles of a primary or
10 secondary amine containing 1 to 24 carbon atoms, propylene oxide, and monostearyl phosphates such as monostearyl alcohol phosphate ester and monostearyl di-alkali metal (e.g., K, Na, and Li) phosphates and phosphate esters. The hydrocarbons such as paraffin and haloparaffin can be utilized in liquid form. The liquid hydrocarbons will be liquid at room temperature and atmospheric pressure, and will have a pour point in the range of
15 about -40°C and about 50°C, and a minimum boiling point not less than about 110°C (atmospheric pressure). It is also known to utilize waxy hydrocarbons, preferably having a melting point below about 100°C. The hydrocarbons constitute a preferred category of suds suppressor for detergent compositions. Hydrocarbon suds suppressors are described, for example, in U.S. Patent 4,265,779, issued May 5, 1981 to Gandolfo et al. The
20 hydrocarbons, thus, include aliphatic, alicyclic, aromatic, and heterocyclic saturated or unsaturated hydrocarbons having from about 12 to about 70 carbon atoms. The term "paraffin," as used in this suds suppressor discussion, is intended to include mixtures of true paraffins and cyclic hydrocarbons.

Another preferred category of non-surfactant suds suppressors comprises silicone
25 suds suppressors. This category includes the use of polyorganosiloxane oils, such as polydimethylsiloxane, dispersions or emulsions of polyorganosiloxane oils or resins, and combinations of polyorganosiloxane with silica particles wherein the polyorganosiloxane is chemisorbed or fused onto the silica. Silicone suds suppressors are well known in the art and are, for example, disclosed in U.S. Patent 4,265,779, issued May 5, 1981 to

 Gandolfo et al and European Patent Application No. 89307851.9, published February 7, 1990, by ~~Starch~~, M. S.

Other silicone suds suppressors are disclosed in U.S. Patent 3,455,839 which relates to compositions and processes for defoaming aqueous solutions by incorporating therein small amounts of polydimethylsiloxane fluids.

Mixtures of silicone and silanated silica are described, for instance, in German Patent Application DOS 2,124,526. Silicone defoamers and suds controlling agents in granular detergent compositions are disclosed in U.S. Patent 3,933,672, Bartolotta et al, and in U.S. Patent 4,652,392, Baginski et al, issued March 24, 1987.

An exemplary silicone based suds suppressor for use herein is a suds suppressing amount of a suds controlling agent consisting essentially of:

- (i) polydimethylsiloxane fluid having a viscosity of from about 20 cs. to about 1,500 cs. at 25°C;
- (ii) from about 5 to about 50 parts per 100 parts by weight of (i) of siloxane resin composed of $(\text{CH}_3)_3\text{SiO}_{1/2}$ units of SiO_2 units in a ratio of from $(\text{CH}_3)_3\text{SiO}_{1/2}$ units and to SiO_2 units of from about 0.6:1 to about 1.2:1; and
- (iii) from about 1 to about 20 parts per 100 parts by weight of (i) of a solid silica gel.

In the preferred silicone suds suppressor used herein, the solvent for a continuous phase is made up of certain polyethylene glycols or polyethylene-polypropylene glycol copolymers or mixtures thereof (preferred), or polypropylene glycol. The primary silicone suds suppressor is branched/crosslinked and preferably not linear.

To illustrate this point further, typical liquid laundry detergent compositions with controlled suds will optionally comprise from about 0.001 to about 1, preferably from about 0.01 to about 0.7, most preferably from about 0.05 to about 0.5, weight % of said silicone uds suppressor, which comprises (1) a nonaqueous emulsion of a primary antifoam agent which is a mixture of (a) a polyorganosiloxane, (b) a resinous siloxane or a silicone resin-producing silicone compound, (c) a finely divided filler material, and (d) a catalyst to promote the reaction of mixture components (a), (b) and (c), to form silanolates; (2) at least one nonionic silicone surfactant; and (3) polyethylene glycol or a

copolymer of polyethylene-polypropylene glycol having a solubility in water at room temperature of more than about 2 weight %; and without polypropylene glycol. Similar amounts can be used in granular compositions, gels, etc. See also U.S. Patents 4,978,471, Starch, issued December 18, 1990, and 4,983,316, Starch, issued January 8, 1991,
5 5,288,431, Huber et al., issued February 22, 1994, and U.S. Patents 4,639,489 and 4,749,740, Aizawa et al at column 1, line 46 through column 4, line 35.

The silicone suds suppressor herein preferably comprises polyethylene glycol and a copolymer of polyethylene glycol/polypropylene glycol, all having an average molecular weight of less than about 1,000, preferably between about 100 and 800. The polyethylene
10 glycol and polyethylene/polypropylene copolymers herein have a solubility in water at room temperature of more than about 2 weight %, preferably more than about 5 weight %.

The preferred solvent herein is polyethylene glycol having an average molecular weight of less than about 1,000, more preferably between about 100 and 800, most preferably between 200 and 400, and a copolymer of polyethylene glycol/polypropylene
15 glycol, preferably PPG 200/PEG 300. Preferred is a weight ratio of between about 1:1 and 1:10, most preferably between 1:3 and 1:6, of polyethylene glycol:copolymer of polyethylene-polypropylene glycol.

The preferred silicone suds suppressors used herein do not contain polypropylene glycol, particularly of 4,000 molecular weight. They also preferably do not contain block
20 copolymers of ethylene oxide and propylene oxide, like PLURONIC L101.

Other suds suppressors useful herein comprise the secondary alcohols (e.g., 2-alkyl alkanols) and mixtures of such alcohols with silicone oils, such as the silicones disclosed in U.S. 4,798,679, 4,075,118 and EP 150,872. The secondary alcohols include the C₆-C₁₆ alkyl alcohols having a C₁-C₁₆ chain. A preferred alcohol is 2-butyl octanol,
25 which is available from Condea under the trademark ISOFOL 12. Mixtures of secondary alcohols are available under the trademark ISALCHEM 123 from Enichem. Mixed suds suppressors typically comprise mixtures of alcohol + silicone at a weight ratio of 1:5 to 5:1.

For any granular compositions to be used in automatic laundry washing machines,
30 suds should not form to the extent that they overflow the washing machine. Suds

suppressors, when utilized, are preferably present in a "suds suppressing amount. By "suds suppressing amount" is meant that the formulator of the composition can select an amount of this suds controlling agent that will sufficiently control the suds to result in a low-sudsing granular detergent for use in automatic laundry washing machines.

5 The compositions herein may comprise from 0% to about 10% of suds suppressor. When utilized as suds suppressors, monocarboxylic fatty acids, and salts therein, will be present typically in amounts up to about 5%, by weight, of the detergent composition. Preferably, from about 0.5% to about 3% of fatty monocarboxylate suds suppressor is utilized. Silicone suds suppressors are typically utilized in amounts up to about 2.0%, by
10 weight, of the detergent composition, although higher amounts may be used. This upper limit is practical in nature, due primarily to concern with keeping costs minimized and effectiveness of lower amounts for effectively controlling sudsing. Preferably from about 0.01% to about 1% of silicone suds suppressor is used, more preferably from about 0.25% to about 0.5%. As used herein, these weight percentage values include any silica that may
15 be utilized in combination with polyorganosiloxane, as well as any adjunct materials that may be utilized. Monostearyl phosphate suds suppressors are generally utilized in amounts ranging from about 0.1% to about 2%, by weight, of the composition. Hydrocarbon suds suppressors are typically utilized in amounts ranging from about 0.01% to about 5.0%, although higher levels can be used. The alcohol suds suppressors are
20 typically used at 0.2%-3% by weight of the finished compositions.

Alkoxylated Polycarboxylates - Alkoxylated polycarboxylates such as those prepared from polyacrylates are useful herein to provide additional grease removal performance. Such materials are described in WO 91/08281 and PCT 90/01815 at p. 4 et seq., incorporated herein by reference. Chemically, these materials comprise
25 polyacrylates having one ethoxy side-chain per every 7-8 acrylate units. The side-chains are of the formula $-(CH_2CH_2O)_m(CH_2)_nCH_3$ wherein m is 2-3 and n is 6-12. The side-chains are ester-linked to the polyacrylate "backbone" to provide a "comb" polymer type structure. The molecular weight can vary, but is typically in the range of about 2000 to about 50,000. Such alkoxylated polycarboxylates can comprise from about 0.05% to
30 about 10%, by weight, of the compositions herein.

Fabric Softeners - Various through-the-wash fabric softeners, especially the impalpable smectite clays of U.S. Patent 4,062,647, Storm and Nirschl, issued December 13, 1977, as well as other softener clays known in the art, can optionally be used typically at levels of from about 0.5% to about 10% by weight in the present compositions to provide fabric softener benefits concurrently with fabric cleaning. Clay softeners can be used in combination with amine and cationic softeners as disclosed, for example, in U.S. Patent 4,375,416, Crisp et al, March 1, 1983 and U.S. Patent 4,291,071, Harris et al, issued September 22, 1981.

The compositions of the present invention may be of an physical form , depending upon the end use of the composition. Typically, the compositions of the present invention may be in the form of liquid, liquid-gel, gel, thixotropic gel, powder, granule (such as, high bulk density granules, or the so-called "fluffy" granules), paste, tablet, bar and the like.

Similarly, the compositions of the present invention can be used in a variety of different applications. Such compositions would include, hard surface cleaners, bleaches, automatic dishwashing, LDL's, HDL's (both aqueous and non-aqueous), heavy duty laundry compositions, laundry-pretreaters, fabric softeners, shampoos, personal cleansers and the like. The compositions of the present invention are especially suitable for use in automatic dishwashing, bleaches and HDL compositions.

The compositions of the present invention may be in the form of a personal cleansing compositions or shampoos. Typically these compositions contain a shampoo composition adjunct ingredient which is preferably selected from anti-dandruff agents (preferably platelet pyridinethione salt crystals, sulfur, octopirox, selenium sulfide, ketoconazole and pyridinethione salts), co-surfactants (preferably selected from anionic surfactant, nonionic surfactant, cationic surfactant, amphoteric surfactant, zwitterionic surfactants, and mixtures thereof), silicone hair conditioning agent, polyalkylene glycols, suspending agent, water, water soluble cationic polymeric conditioning agents, hydrocarbon conditioning agents, foam boosters, preservatives, thickeners, cosurfactants, dyes, perfumes, solvents, styling polymers, anti-static agents, deposition polymers, styling polymers and solvent, dispersed phase polymers, non-volatile hydrocarbons conditioning

agents, silicone conditioning agents, suspending agent, cationic spreading agents phase separation initiators and pediculocides and mixtures thereof. These and other suitable materials for incorporation into the shampoo compositions can be found in U.S. Patent applications Serial Nos. 60/061,975 filed on October 17, 1997 (Docket No. 6882P), and 5 60/061,916 filed on October 17, 1997 (Docket No. 6884P).

The compositions of the present invention can also be in the form of LDL compositions. These LDL compositions include, in addition to those detailed previously, additives typically used in LDL formulations, such as diamines, divalent ions, suds boosting polymers, soil release polymers, polymeric dispersants, polysaccharides, 10 abrasives, bactericides, tarnish inhibitors, builders, enzymes, dyes, perfumes, thickeners, antioxidants, processing aids, suds boosters, buffers, antifungal or mildew control agents, insect repellants, anti-corrosive aids, and chelants.

The compositions of the present invention may be in the form of a non-aqueous, liquid, heavy-duty detergent compositions in the form of a stable suspension of solid, 15 substantially insoluble particulate material dispersed throughout a structured, surfactant-containing liquid phase.

Suitable types of non-aqueous surfactant liquids which can be used to form the liquid phase of the compositions herein include the alkoxyated alcohols, ethylene oxide (EO)-propylene oxide (PO) block polymers, polyhydroxy fatty acid amides, 20 alkylpolysaccharides, and the like.

The liquid phase of the HDL compositions herein may also comprise one or more non-surfactant, non-aqueous organic solvents. Suitable types of low-polarity solvents useful in the non-aqueous liquid detergent compositions herein do include non-vicinal C₄-C₈ alkylene glycols, alkylene glycol mono lower alkyl ethers, lower molecular weight 25 polyethylene glycols, lower molecular weight methyl esters and amides, and the like. Mixtures of non-surfactant, non-aqueous organic solvents and non-aqueous surfactant liquids are also contemplated.

The non-aqueous liquid phase of the HDL compositions of this invention is prepared by combining with the non-aqueous organic liquid diluents hereinbefore described a 30 surfactant which is generally, but not necessarily, selected to add structure to the non-

aqueous liquid phase of the detergent compositions herein. Structuring surfactants can be of the anionic, nonionic, cationic, and/or amphoteric types.

The most preferred type of anionic surfactant for use as a structurant in the HDL compositions herein comprises the linear alkyl benzene sulfonate (LAS) surfactants.

5 The non-aqueous HDL compositions herein preferably comprise a solid phase particulate material which is dispersed and suspended within the liquid phase. Generally such particulate material will range in size from about 0.1 to 1500 microns, more preferably from about 0.1 to 900 microns. Most preferably, such material will range in size from about 5 to 200 microns.

10 The ether-capped poly(oxyalkylated) alcohol surfactants of the present invention may also be incorporated in to aqueous HDL compositions.

As it was mentioned previously the surfactants of the present invention may be included in a fabric softening composition. Suitable materials for incorporation into the fabric softening compositions in addition to the surfactants of the present invention can be
15 found in U.S. Patent applications Serial Nos. 5,830,845, granted on November 3, 1998; 5,929,025, granted on July 27, 1999; 5,877,745, granted on March 2, 1999; 5,977,055, granted on November 2, 1999; 5,854,200, granted on December 29, 1998; and 5,686,376, Rusche et al., granted on November 2, 1999.

The particulate material utilized herein can comprise one or more types of detergent
20 composition components which in particulate form are substantially insoluble in the non-aqueous liquid phase of the composition. The types of particulate materials which can be utilized are described are peroxygen bleaching agent, organic builder, inorganic alkalinity source (preferably include water-soluble alkali metal carbonates, bicarbonates, borates, pyrophosphates, orthophosphates, polyphosphates phosphonates, silicates and
25 metasilicates), colored speckles and mixtures thereof.

The present invention also comprises aqueous based liquid detergent compositions. The aqueous liquid detergent compositions of the present invention comprise a surfactant system which preferably contains one or more deterative co-surfactants in addition to the branched surfactants disclosed above. The additional co-surfactants can be selected from
30 nonionic deterative surfactant, anionic deterative surfactant, zwitterionic deterative

surfactant, amine oxide deterative surfactant, and mixtures thereof. The surfactant system typically comprises from about 5% to about 70%, preferably from about 15% to about 30%, by weight of the detergent composition. These surfactants are hereinbefore described.

5 In addition to the liquid and solid phase components as hereinbefore described, the aqueous and non-aqueous based detergent compositions can, and preferably will, contain various other optional components. Such optional components may be in either liquid or solid form. The optional components may either dissolve in the liquid phase or may be dispersed within the liquid phase in the form of fine particles or droplets. Suitable
10 optional material includes for example chelating agents, enzymes, builders, bleach catalysts, bleach activators, thickeners, viscosity control agents and/or dispersing agents suds boosters, liquid bleach activator, dye transfer inhibitors, solvents, suds suppressors, structure elasticizing agent, anti redeposition agents, to exemplify but a few possible optional ingredients. Some of the materials which may optionally be utilized in the
15 compositions herein are described in greater detail. Further details on suitable adjunct ingredients to HDL compositions, methods of preparing same and use in the compositions can be found in U.S. Patent applications Serial Nos. 60/062,087 (Docket No. 6876P), and 60/061,924 (Docket No. 6877P).

Other Ingredients - The detergent compositions will further preferably comprise
20 one or more deterative adjuncts selected from the following: electrolytes (such as sodium chloride), polysaccharides, abrasives, bactericides, tarnish inhibitors, dyes, antifungal or mildew control agents, insect repellents, perfumes, hydrotropes, thickeners, processing aids, suds boosters, anti-corrosive aids, stabilizers and antioxidants. A wide variety of other ingredients useful in detergent compositions can be included in the compositions
25 herein, including other active ingredients, carriers, hydrotropes, antioxidants, processing aids, dyes or pigments, solvents for liquid formulations, etc. If high sudsing is desired, suds boosters such as the C₁₀-C₁₆ alkanolamides can be incorporated into the compositions, typically at 1%-10% levels. The C₁₀-C₁₄ monoethanol and diethanol amides illustrate a typical class of such suds boosters. Use of such suds boosters with

high sudsing adjunct surfactants such as the amine oxides, betaines and sultaines noted above is also advantageous.

An antioxidant can be optionally added to the detergent compositions of the present invention. They can be any conventional antioxidant used in detergent
5 compositions, such as 2,6-di-tert-butyl-4-methylphenol (BHT), carbamate, ascorbate, thiosulfate, monoethanolamine(MEA), diethanolamine, triethanolamine, etc. It is preferred that the antioxidant, when present, be present in the composition from about 0.001% to about 5% by weight.

Various deterative ingredients employed in the present compositions optionally can
10 be further stabilized by absorbing said ingredients onto a porous hydrophobic substrate, then coating said substrate with a hydrophobic coating. Preferably, the deterative ingredient is admixed with a surfactant before being absorbed into the porous substrate. In use, the deterative ingredient is released from the substrate into the aqueous washing liquor, where it performs its intended deterative function.

15 To illustrate this technique in more detail, a porous hydrophobic silica (trademark SIPERNAT D10, DeGussa) is admixed with a proteolytic enzyme solution containing 3%-5% of C₁₃₋₁₅ ethoxylated alcohol (EO 7) nonionic surfactant. Typically, the enzyme/surfactant solution is 2.5 X the weight of silica. The resulting powder is dispersed with stirring in silicone oil (various silicone oil viscosities in the range of 500-
20 12,500 can be used). The resulting silicone oil dispersion is emulsified or otherwise added to the final detergent matrix. By this means, ingredients such as the aforementioned enzymes, bleaches, bleach activators, bleach catalysts, photoactivators, dyes, fluorescers, fabric conditioners and hydrolyzable surfactants can be "protected" for use in detergents, including liquid laundry detergent compositions.

25 Further, the compositions may optionally comprises a hydrotrope. Suitable hydrotropes include sodium, potassium, ammonium or water-soluble substituted ammonium salts of toluene sulfonic acid, naphthalene sulfonic acid, cumene sulfonic acid, xylene sulfonic acid.

The manufacture of LDL compositions which comprise a non-aqueous carrier
30 medium can be prepared according to the disclosures of U.S. Patents 4,753,570;

4,767,558; 4,772,413; 4,889,652; 4,892,673; GB-A-2,158,838; GB-A-2,195,125; GB-A-2,195,649; U.S. 4,988,462; U.S. 5,266,233; EP-A-225,654 (6/16/87); EP-A-510,762 (10/28/92); EP-A-540,089 (5/5/93); EP-A-540,090 (5/5/93); U.S. 4,615,820; EP-A-565,017 (10/13/93); EP-A-030,096 (6/10/81), incorporated herein by reference. Such
5 compositions can contain various particulate deterative ingredients stably suspended therein. Such non-aqueous compositions thus comprise a LIQUID PHASE and, optionally but preferably, a SOLID PHASE, all as described in more detail hereinafter and in the cited references.

The LDL compositions of this invention can be used to form aqueous washing
10 solutions for use hand dishwashing. Generally, an effective amount of such LDL compositions is added to water to form such aqueous cleaning or soaking solutions. The aqueous solution so formed is then contacted with the dishware, tableware, and cooking utensils.

An effective amount of the LDL compositions herein added to water to form
15 aqueous cleaning solutions can comprise amounts sufficient to form from about 500 to 20,000 ppm of composition in aqueous solution. More preferably, from about 800 to 5,000 ppm of the detergent compositions herein will be provided in aqueous cleaning liquor.

The mean particle size of the components of granular compositions in accordance
20 with the invention should preferably be such that no more than 5% of particles are greater than 1.7mm in diameter and not more than 5% of particles are less than 0.15mm in diameter.

The term mean particle size as defined herein is calculated by sieving a sample of the composition into a number of fractions (typically 5 fractions) on a series of Tyler
25 sieves. The weight fractions thereby obtained are plotted against the aperture size of the sieves. The mean particle size is taken to be the aperture size through which 50% by weight of the sample would pass.

The granular laundry compositions in accordance with the present invention typically has a bulk density of from 100 g/litre to 1400 g/litre, more preferably from 300
30 g/litre to 1200 g/litre, from 650 g/litre to 1000 g/litre.

High Density Detergent Composition Processes

Various means and equipment are available to prepare high density (i.e., greater than about 550, preferably greater than about 650, grams/liter or "g/l"), high solubility, free-flowing, granular detergent compositions according to the present invention. Current commercial practice in the field employs spray-drying towers to manufacture granular laundry detergents which often have a density less than about 500 g/l. In this procedure, an aqueous slurry of various heat-stable ingredients in the final detergent composition are formed into homogeneous granules by passage through a spray-drying tower, using conventional techniques, at temperatures of about 175°C to about 225°C. However, if spray drying is used as part of the overall process herein, additional or alternative process steps as described hereinafter must be used to obtain the level of density (i.e., > 650 g/l) required by modern compact, low dosage detergent products.

For example, spray-dried granules from a tower can be densified further by loading a liquid such as water or a nonionic surfactant into the pores of the granules and/or subjecting them to one or more high speed mixer/densifiers. A suitable high speed mixer/densifier for this process is a device marketed under the tradename "Lödige CB 30" or "Lödige CB 30 Recycler" which comprises a static cylindrical mixing drum having a central rotating shaft with mixing/cutting blades mounted thereon. In use, the ingredients for the detergent composition are introduced into the drum and the shaft/blade assembly is rotated at speeds in the range of 100-2500 rpm to provide thorough mixing/densification. See Jacobs et al, U.S. Patent 5,149,455, issued September 22, 1992, and U.S. Patent 5,565,422, issued October 15, 1996 to Del Greco et al. Other such apparatus includes the devices marketed under the tradename "Shugi Granulator" and under the tradename "Drais K-TTP 80).

Another process step which can be used to densify further spray-dried granules involves treating the spray-dried granules in a moderate speed mixer/densifier. Equipment such as that marketed under the tradename "Lödige KM" (Series 300 or 600) or "Lödige Ploughshare" mixer/densifiers are suitable for this process step. Such equipment is typically operated at 40-160 rpm. The residence time of the detergent ingredients in the moderate speed mixer/densifier is from about 0.1 to 12 minutes

conveniently measured by dividing the steady state mixer/densifier weight by the throughput (e.g., Kg/hr). Other useful equipment includes the device which is available under the tradename "Drais K-T 160". This process step which employs a moderate speed mixer/densifier (e.g. Lödige KM) can be used by itself or sequentially with the
5 aforementioned high speed mixer/densifier (e.g. Lödige CB) to achieve the desired density. Other types of granules manufacturing apparatus useful herein include the apparatus disclosed in U.S. Patent 2,306,898, to G. L. Heller, December 29, 1942.

While it may be more suitable to use the high speed mixer/densifier followed by the low speed mixer/densifier, the reverse sequential mixer/densifier configuration also can
10 be used. One or a combination of various parameters including residence times in the mixer/densifiers, operating temperatures of the equipment, temperature and/or composition of the granules, the use of adjunct ingredients such as liquid binders and flow aids, can be used to optimize densification of the spray-dried granules in the process of the invention. By way of example, see the processes in Appel et al, U.S. Patent
15 5,133,924, issued July 28, 1992; Delwel et al, U.S. Patent 4,637,891, issued January 20, 1987; Kruse et al, U.S. Patent 4,726,908, issued February 23, 1988; and, Bortolotti et al, U.S. Patent 5,160,657, issued November 3, 1992.

In those situations in which particularly heat sensitive or highly volatile detergent ingredients are to be incorporated into the final detergent composition, processes which
20 do not include spray drying towers are preferred. The formulator can eliminate the spray-drying step by feeding, in either a continuous or batch mode, starting detergent ingredients directly into mixing equipment that is commercially available. One particularly preferred embodiment involves charging a surfactant paste and an anhydrous material into a high speed mixer/densifier (e.g. Lödige CB) followed by a moderate speed mixer/densifier
25 (e.g. Lödige KM) to form high density detergent agglomerates. See Capeci et al, U.S. Patent 5,366,652, issued November 22, 1994 and Capeci et al, U.S. Patent 5,486,303, issued January 23, 1996. Optionally, the liquid/solids ratio of the starting detergent ingredients in such a process can be selected to obtain high density agglomerates that are more free flowing and crisp. See Capeci et al, U.S. Patent 5,565,137, issued October 15,
30 1996.

Optionally, the process may include one or more recycle streams of undersized particles produced by the process which are fed back to the mixer/densifiers for further agglomeration or build-up. The oversized particles produced by this process can be sent to grinding apparatus and then fed back to the mixing/densifying equipment. These additional recycle process steps facilitate build-up agglomeration of the starting detergent ingredients resulting in a finished composition having a uniform distribution of the desired particle size (400-700 microns) and density (> 550 g/l). See Capeci et al, U.S. Patent 5,516,448, issued May 14, 1996 and Capeci et al, U.S. Patent 5,489,392, issued February 6, 1996. Other suitable processes which do not call for the use of spray-drying towers are described by Bollier et al, U.S. Patent 4,828,721, issued May 9, 1989; Beerse et al, U.S. Patent 5,108,646, issued April 28, 1992; and, Jolicoeur, U.S. Patent 5,178,798, issued January 12, 1993.

In yet another embodiment, a high density detergent composition using a fluidized bed mixer. In this process, the various ingredients of the finished composition are combined in an aqueous slurry (typically 80% solids content) and sprayed into a fluidized bed to provide the finished detergent granules. Prior to the fluidized bed, this process can optionally include the step of mixing the slurry using the aforementioned Lödige CB mixer/densifier or a "Flexomix 160" mixer/densifier, available from Shugi. Fluidized bed or moving beds of the type available under the tradename "Escher Wyss" can be used in such processes.

Another suitable process which can be used herein involves feeding a liquid acid precursor of an anionic surfactant, an alkaline inorganic material (e.g. sodium carbonate) and optionally other detergent ingredients into a high speed mixer/densifier so as to form particles containing a partially or totally neutralized anionic surfactant salt and the other starting detergent ingredients. Optionally, the contents in the high speed mixer/densifier can be sent to a moderate speed mixer/densifier (e.g. Lödige KM) for further mixing resulting in the finished high density detergent composition. See Appel et al, U.S. Patent 5,164,108, issued November 17, 1992.

Optionally, high density detergent compositions according to the invention can be produced by blending conventional or densified spray-dried detergent granules with

detergent agglomerates in various proportions (e.g. a 60:40 weight ratio of granules to agglomerates) produced by one or a combination of the processes discussed herein. See U.S. Patent 5,569,645, issued October 29, 1996 to Dinniwell et al. Additional adjunct ingredients such as enzymes, perfumes, brighteners and the like can be sprayed or
5 admixed with the agglomerates, granules or mixtures thereof produced by the processes discussed herein.

Laundry washing method

Machine laundry methods herein typically comprise treating soiled laundry with an aqueous wash solution in a washing machine having dissolved or dispensed therein an
10 effective amount of a machine laundry detergent composition in accord with the invention. By an effective amount of the detergent composition it is here meant from 40g to 300g of product dissolved or dispersed in a wash solution of volume from 5 to 65 litres, as are typical product dosages and wash solution volumes commonly employed in conventional machine laundry methods.

15 As noted, surfactants are used herein in detergent compositions, preferably in combination with other deterative surfactants, at levels which are effective for achieving at least a directional improvement in cleaning performance. In the context of a fabric laundry composition, such "usage levels" can vary widely, depending not only on the type and severity of the soils and stains, but also on the wash water temperature, the volume of
20 wash water and the type of washing machine.

Packaging for the compositions

Commercially marketed executions of the compositions can be packaged in any suitable container including those constructed from paper, cardboard, plastic materials and any suitable laminates. A preferred packaging execution is described in European
25 Application No. 94921505.7.

The compositions herein may be packaged in a variety of suitable detergent packaging known to those skilled in the art. The liquid compositions are preferably packaged in conventional detergent plastic bottles.

The following examples are illustrative of the present invention, but are not meant
30 to limit or otherwise define its scope. The ether-capped poly(oxyalkylated) alcohol

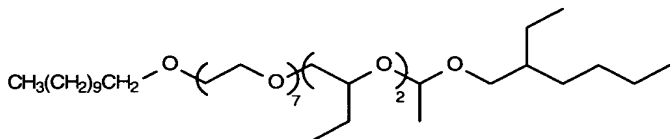
surfactant of the present invention is not limited in use to cleaning applications. They may be used in other applications, such as wetting agents, antifoaming agents, drilling muds, etc, in a wide range of fields, such as in biocides, pharmaceuticals, etc. Further examples of possible application for these surfactants can be found in "Nonionic

5 Surfactants" edited by Martin J. Schinck, Surfactant Science Series, Mancel Dekker, NY, Volume 1; "Nonionic Surfactants: Physical Chemistry" edited by Martin J. Schinck, Surfactant Science Series, Mancel Dekker, NY, Volume 23; "Nonionic Surfactants: Polyoxyalkylen Block Copolymers" edited by Vaughn M. Nace, Surfactant Science

10 Series, Mancel Dekker, NY, Volume 60; and L.G. Lundsted and I.R. Schmolka, in "Block and Graft Copolymerization", Vol. 2 (R.J. Ceresa, ed.), John Wiley & Sons, Ltd., London, 1976, pp.113-272. All parts, percentages and ratios used herein are expressed as percent weight unless otherwise specified.

EXAMPLES

Example 1



Preparation of C₁₁H₂₃EO₇BO₂-2-ethylhexyl acetal

Neodol 1-7 (20.00 g, 41.6 mmol) is placed into a 500 ml three-necked round-bottomed flask, fitted with a heating mantle, magnetic stirrer, internal thermometer and argon inlet and dried under vacuum at 75°C. After releasing the vacuum with argon, sodium metal

20 (0.05 g, 2.1 mmol) is added and the mixture stirred for 1 h at 120°C. After increasing the reaction temperature to 140°C, 1,2-epoxybutane (6.00 g, 83.2 mmol) is added dropwise over 30 minutes. After the addition is complete the mixture is stirred for an additional 1 h at 140°C. The solution is cooled to 90°C and neutralized with concentrated HCl. After removing water and the last traces of 1,2-epoxybutane under vacuum and cooling to

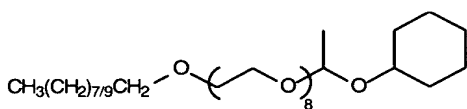
25 ambient, methylene chloride (200 ml) and 2-ethylhexyl vinyl ether (19.49 g, 124.7 mmol) are added. The mixture is cooled to 0°C and pyridinium p-toluenesulfonate (0.42 g, 1.7 mmol) is added. The mixture is first stirred 4 h at 0°C and then 18 h at ambient. After diluting with diethyl ether (200 ml), the mixture is washed twice with saturated sodium

bicarbonate and the organic layer dried with sodium sulfate/potassium carbonate. The product was concentrated by rotary evaporation and dried under vacuum in the presence of potassium carbonate to yield a yellow liquid.

Example 2

- 5 Examples 2(a) to (i) are illustrative of some of the possible catalysts, work up options and relative amounts the starting materials that can be used in the present invention.

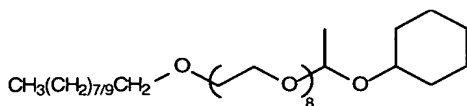
Example 2(a)



- 10 Preparation of $C_{9/11}H_{19/23}EO_8$ -cyclohexyl acetal

Neodol 91-8 (20.00 g, 39.1 mmol) is placed into a 250 ml three-necked round-bottomed flask, fitted with a heating mantle, magnetic stirrer, internal thermometer and argon inlet and dried under vacuum at 75°C. After cooling to ambient and releasing the vacuum with argon, methylene chloride (100 ml) and cyclohexyl vinyl ether (5.43 g, 43.01 mmol) are added. The mixture is cooled to 0°C and pyridinium p-toluenesulfonate (0.43 g, 1.6 mmol) is introduced into the flask. The mixture is first stirred 4 h at 0°C and then 18 h at ambient. The product mixture is then washed twice with saturated sodium bicarbonate and the organic layer dried over sodium carbonate, concentrated by rotary evaporation and further stripped under vacuum at 60°C (0.1 mmHg) in the presence of potassium carbonate to yield a liquid.

Example 2(b)

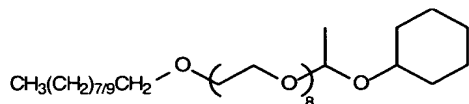


Preparation of $C_{9/11}H_{19/23}EO_8$ -cyclohexyl acetal

- 25 Neodol 91-8 (20.00 g, 39.1 mmol) and poly(4-vinylpyridinium p-toluenesulfonate) (0.43 g) are introduced into a 250 ml three-necked round-bottomed flask, fitted with a heating mantle, magnetic stirrer, internal thermometer and argon inlet and dried under vacuum at 75°C. After cooling to ambient and releasing the vacuum with argon, cyclohexyl vinyl

ether (4.94 g, 39.1 mmol) is added. The mixture is heated to 70-95°C overnight. The product mixture is filtered to yield a liquid.

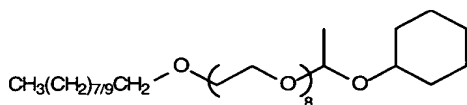
Example 2(c)



5 Preparation of C_{9/11}H_{19/23}EO₈-cyclohexyl acetal

Neodol 91-8 (20.00 g, 39.1 mmol) and poly(4-vinylpyridinium p-toluenesulfonate) (0.43 g) are introduced into a 250 ml three-necked round-bottomed flask, fitted with a heating mantle, magnetic stirrer, internal thermometer and argon inlet and dried under vacuum at 75°C. After cooling to ambient and releasing the vacuum with argon, cyclohexyl vinyl ether (4.94 g, 39.1 mmol) is added. The mixture is heated to 70-95°C overnight. The product mixture is separated from the catalyst by centrifugation to yield a liquid.

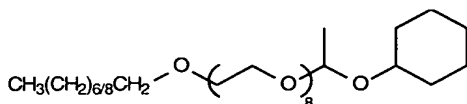
Example 2(d)



15 Preparation of C_{9/11}H_{19/23}EO₈-cyclohexyl acetal

Neodol 91-8 (20.00 g, 39.1 mmol) and poly(4-vinylpyridinium p-toluenesulfonate) (0.43 g) are introduced into a 250 ml three-necked round-bottomed flask, fitted with a heating mantle, magnetic stirrer, internal thermometer and argon inlet and dried under vacuum at 75°C. After cooling to ambient and releasing the vacuum with argon, cyclohexyl vinyl ether (4.94 g, 39.1 mmol) is added. The mixture is heated to 70-95°C overnight. The product mixture is washed with 20% potassium carbonate solution, dried and filtered to yield a liquid.

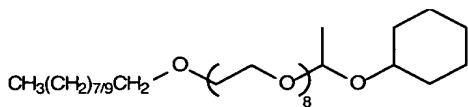
Example 2(e)



25 Preparation of C_{8/10}H_{17/21}EO₈-cyclohexyl acetal

- Alcohol ethoxylate $C_{8/10}H_{17/21}EO_8$ (20.00 g, 40.2 mmol) and poly(4-vinylpyridinium chloride) (2.0 g) are introduced into a 250 ml three-necked round-bottomed flask, fitted with a heating mantle, magnetic stirrer, internal thermometer and argon inlet and dried under vacuum at 75°C. After cooling to ambient and releasing the vacuum with argon,
- 5 cyclohexyl vinyl ether (5.07 g, 40.2 mmol) is added. The mixture is heated to 70-95°C overnight. The product mixture is filtered to yield a liquid.

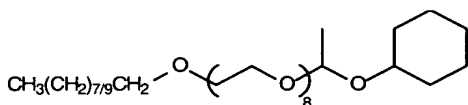
Example 2(f)



Preparation of $C_{9/11}H_{19/23}EO_8$ -cyclohexyl acetal

- 10 Neodol 91-8 (20.00 g, 39.1 mmol) and poly(4-vinylpyridinium p-toluenesulfonate) (7.82 g) are introduced into a 250 ml three-necked round-bottomed flask, fitted with a heating mantle, magnetic stirrer, internal thermometer and argon inlet and dried under vacuum at 75°C. After cooling to ambient and releasing the vacuum with argon, acetone (150 mL) and cyclohexyl vinyl ether (4.94 g, 39.1 mmol) are added. The mixture is stirred for three
- 15 days, filtered and concentrated by rotary evaporation to yield a liquid.

Example 2(g)

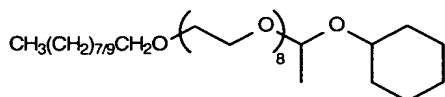


Preparation of $C_{9/11}H_{19/23}EO_8$ -cyclohexyl acetal

- 20 Neodol 91-8 (20.00 g, 39.1 mmol) is placed into a 250 ml three-necked round-bottomed flask, fitted with a heating mantle, magnetic stirrer, internal thermometer and argon inlet and dried under vacuum at 75°C. After cooling to ambient and releasing the vacuum with argon, methylene chloride (100 ml) and cyclohexyl vinyl ether (4.84 g, 38.4 mmol) are added. The mixture is cooled to 0°C and pyridinium p-toluenesulfonate (0.39 g, 1.5 mmol) is introduced into the flask. The mixture is first stirred 4 h at 0°C and then 18 h at
- 25 ambient. The product mixture is then washed twice with saturated sodium bicarbonate and the organic layer dried over sodium carbonate, concentrated by rotary evaporation and

further stripped under vacuum at 60°C (0.1 mmHg) in the presence of potassium carbonate to yield a liquid.

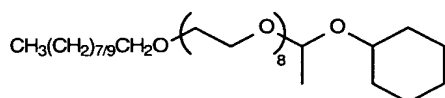
Example 2(h)



5 Preparation of C_{9/11}H_{19/23}EO₈-cyclohexyl acetal

Neodol 91-8 (20.00 g, 39.1 mmol) is placed into a 250 ml three-necked round-bottomed flask, fitted with a heating mantle, magnetic stirrer, internal thermometer and argon inlet and dried under vacuum at 75°C. After cooling to ambient, cyclohexyl vinyl ether (5.04 g, 39.9 mmol) is added. *p*-Toluenesulfonic acid monohydrate (0.112 g, 0.59 mmol) is added to the mixture and stirred to dissolve. An exotherm is observed starting from 22°C and ending at 30°C, with the development of a precipitate. After 16 minutes of reaction time, the reaction pH is adjusted to ≥7 with triethanolamine, filtered and then stripped in a Kugelrohr oven (50°C, 0.1 mm Hg) to yield a quantitative amount of a near colorless liquid.

15 Example 2(i)

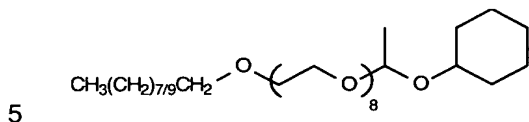


Preparation of C_{9/11}H_{19/23}EO₈-cyclohexyl acetal

Neodol 91-8 (900.0 g, 1.76 mol) is placed into a 3 L three-necked rounded bottomed flask, fitted with a heating mantel, mechanical stirrer, internal thermometer, and vacuum/argon take-off adapter. The contents are dried under vacuum at 80 °C for 30 min. A portion of the dry Neodol 91-8 (20 g) is set aside after the contents are cooled to room temperature. Cyclohexylvinyl ether (217.82 g, 1.73 mol) is then added to the reaction mixture. The reagents are cooled to about 10 °C at which point methanesulfonic acid (1.80 mL) and the 20 g portion of Neodol set aside are combined and added to the reaction mixture via syringe, subsurface, in one portion. The reaction mixture exotherms, ice bath controlled, to 22 °C. After 1h, the mixture is quenched with 15% sodium carbonate solution (35 mL). The mixture is placed under vacuum by stripping in a

Kugelrohr oven (25 °C, 0.1 mm Hg) for 10 min. The product is filtered to yield a quantitative amount of a near colorless liquid.

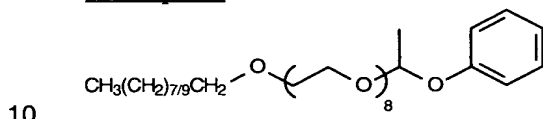
Example 3



Preparation of C_{9/11}H_{19/23}EO₈-cyclohexyl acetal

The procedure of Example 2(i) is repeated with the substitution of Neodol 91-8 for Neodol 1-7.

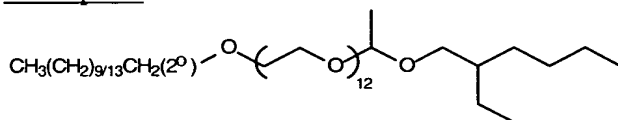
Example 4



Preparation of C_{9/11}H_{19/23}EO₈-benzyl acetal

The procedure of Example 3 is repeated with the substitution of benzyl vinyl ether for cyclohexyl vinyl ether.

Example 5

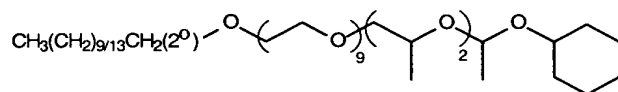


Preparation of C_{11/15}H_{23/31}EO₁₂-2-ethylhexyl acetal

The procedure of Example 2(i) is repeated with the substitution of 2-ethylhexyl vinyl ether for cyclohexyl vinyl ether and Tergitol-15-S-12 for Neodol 1-7.

20

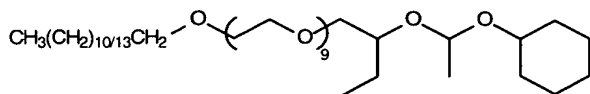
Example 6



Preparation C_{11/15}H_{23/31}EO₉PO₂-cyclohexyl acetal

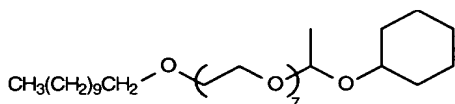
The procedure of Example 1 is repeated with the substitution of propylene oxide for 1,2-epoxybutane, cyclohexyl vinyl ether for 2-ethylhexyl vinyl ether, and Tergitol 15-S-9 for Neodol 1-7.

25

Example 7

Preparation of $C_{12/15}H_{25/31}EO_9BO_1$ -cyclohexyl acetal

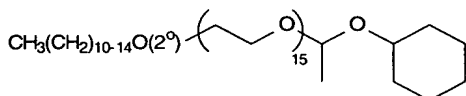
- 5 The procedure of Example 1 is repeated with the substitution of cyclohexyl vinyl ether for 2-ethylhexyl vinyl ether and Neodol 25-9 for Neodol 1-7.

Example 8

- 10 Preparation of $C_{11}H_{23}EO_7$ -cyclohexyl acetal

Neodol 1-7 (50.00 g, 104.0 mmol) is placed into a 1000 ml three-necked round-bottomed flask, fitted with a heating mantle, magnetic stirrer, internal thermometer and argon inlet and dried under vacuum at 75°C. After cooling to ambient and releasing the vacuum with argon, methylene chloride (500 ml) and cyclohexyl vinyl ether (6.55g, 51.9 mmol) are added. The mixture is cooled to 0°C and pyridinium *p*-toluenesulfonate (1.04 g, 4.2 mmol) is introduced into the flask. The mixture is first stirred 4 h at 0°C and then 18 h at ambient. The product mixture is then washed twice with saturated sodium bicarbonate and the organic layer dried with magnesium sulfate, concentrated by rotary evaporation and further stripped under vacuum at 60°C (0.1 mmHg) to yield a liquid.

- 20 Example 9



Preparation of $C_{11/15}H_{23/31}EO_{15}$ -cyclohexyl acetal

Tergitol 15-S-15 (100.0 g, 193.8 mmol) is placed into a 250 ml three-necked round-bottomed flask, fitted with a heating mantle, magnetic stirrer, internal thermometer, and vacuum/argon take-off adapter. The contents are dried under vacuum at 80 °C for 10 min. A portion of the dry Tergitol 15-S-15 (2 g) is set aside after the contents are cooled to room temperature. Cyclohexyl vinyl ether (24.21 g, 191.9 mmol) is then added to the

reaction mixture. The reagents are cooled to about 15 °C at which point methanesulfonic acid (0.28 g, 2.9 mmol) and the 2 g portion of Tergitol 15-S-15 set aside are combined and added to the reaction mixture via syringe, subsurface and in one portion. The reaction mixture exotherms to 40 °C. After 5 minutes, the reaction pH is adjusted to ≥ 7 with 15% sodium carbonate. The mixture is placed under vacuum by stripping in a Kugelrohr oven (50 °C, 0.1 mm Hg) for 10 min. The product is filtered to yield a quantitative amount of a near colorless liquid.

The following examples are illustrative of the present invention, but are not meant to limit or otherwise define its scope. The ether-capped poly(oxyalkylated) alcohol surfactant produced by the process of the present invention may be used in other applications, such as a wetting agents, antifoaming agents, drilling muds, etc., in a wide range of fields, such as in biocides, pharmaceuticals, etc. Further examples of possible application for these surfactants can be found in "Nonionic Surfactants" edited by Martin J. Schinck, Surfactant Science Series, Mancel Dekker, NY, Volume 1; "Nonionic Surfactants: Physical Chemistry" edited by Martin J. Schinck, Surfactant Science Series, Mancel Dekker, NY, Volume 23; "Nonionic Surfactants: Polyoxyalkylen Block Copolymers" edited by Vaughn M. Nace, Surfactant Science Series, Mancel Dekker, NY, Volume 60; and L.G. Lundsted and I.R. Schmolka, in "Block and Graft Copolymerization", Vol. 2 (R.J. Ceresa, ed.), John Wiley & Sons, Ltd., London, 1976, pp.113-272. All parts, percentages and ratios used herein are expressed as percent weight unless otherwise specified.

FORMULATION EXAMPLES

In the following Examples, the abbreviations for the various ingredients used for the compositions have the following meanings.

25	LAS	Sodium linear C ₁₂ alkyl benzene sulfonate
	MBAS _x	Mid-chain branched primary alkyl (average total carbons = x) sulfate
	MBAE _x S _z	Mid-chain branched primary alkyl (average total carbons = z) ethoxylate (average EO = x) sulfate, sodium salt
30		

	MBAE _x	Mid-chain branched primary alkyl (average total carbons = x) ethoxylate (average EO = 8)
	TFAA	C16-18 alkyl N-methyl glucamide
5	C _{xy} EzS	Sodium C _{1x} -C _{1y} branched alkyl sulfate condensed with z moles of ethylene oxide
	C _{xy} FA	C _{1x} -C _{1y} fatty acid
	C _{xy} Ez	A C _{1x-1y} branched primary alcohol condensed with an average of z moles of ethylene oxide
	C24 N-Me Glucamide	C ₁₂ -C ₁₄ N-methyl glucamide
10	C _x APA	Alkyl amido propyl amine
	Citric acid	Anhydrous citric acid
	Carbonate	Anhydrous sodium carbonate with a particle size between 200µm and 900µm
15	Citrate	Tri-sodium citrate dihydrate of activity 86.4% with a particle size distribution between 425µm and 850 µm
	Protease	Proteolytic enzyme of activity 4KNPU/g sold by NOVO Industries A/S under the tradename Savinase
	Cellulase	Cellulytic enzyme of activity 1000 CEVU/g sold by NOVO Industries A/S under the tradename Carezyme
20	Amylase	Amylolytic enzyme of activity 60KNU/g sold by NOVO Industries A/S under the tradename Termamyl 60T
	Lipase	Lipolytic enzyme of activity 100kLU/g sold by NOVO Industries A/S under the tradename Lipolase
25	Endolase	Endoglunase enzyme of activity 3000 CEVU/g sold by NOVO Industries A/S
	PB1	Anhydrous sodium perborate bleach of nominal formula NaBO ₂ .H ₂ O ₂
	NOBS	Nonanoyloxybenzene sulfonate in the form of the sodium salt.

	DTPMP	Diethylene triamine penta (methylene phosphonate), marketed by Monsanto under the Trade name Dequest 2060
	MEA	Monoethanolamine
	PG	Propanediol
5	EtOH	Ethanol
	Brightener 1	Disodium 4,4'-bis(2-sulphostyryl)biphenyl
	Brightener 2	Disodium 4,4'-bis(4-anilino-6-morpholino-1.3.5-triazin-2-yl)amino) stilbene-2:2'-disulfonate.
10	Silicone antifoam	Polydimethylsiloxane foam controller with siloxane-oxyalkylene copolymer as dispersing agent with a ratio of said foam controller to said dispersing agent of 10:1 to 100:1.
	NaOH	Solution of sodium hydroxide
	DTPA	Diethylene triamine pentaacetic acid
	NaTS	Sodium toluene sulfonic acid
15	Fatty Acid (C12/14)	C12-C14 fatty acid
	Fatty Acid (TPK)	Topped palm kernel fatty acid
	Fatty Acid (RPS)	Rapeseed fatty acid
	Borax	Na tetraborate decahydrate
	PAA	Polyacrylic Acid (mw = 4500)
20	PEG	Polyethylene glycol (mw=4600)
	MES	Alkyl methyl ester sulfonate
	SAS	Secondary alkyl sulfate
	NaPS	Sodium paraffin sulfonate
	C45AS	Sodium C ₁₄ -C ₁₅ linear alkyl sulfate
25	C _x yAS	Sodium C _{1x} -C _{1y} alkyl sulfate (or other salt if specified)
	AQA	R ₂ .N ⁺ (CH ₃) _x ((C ₂ H ₄ O) _y H) _z with R ₂ = C ₈ - C ₁₈ where x + z = 3, x = 0 to 3, z = 0 to 3, y = 1 to 15.
	STPP	Anhydrous sodium tripolyphosphate

	Zeolite A	Hydrated Sodium Aluminosilicate of formula $\text{Na}_{12}(\text{Al}_{10}\text{SiO}_2)_{12} \cdot 27\text{H}_2\text{O}$ having a primary particle size in the range from 0.1 to 10 micrometers
	NaSKS-6	Crystalline layered silicate of formula $\delta\text{-Na}_2\text{Si}_2\text{O}_5$
5	Bicarbonate	Anhydrous sodium bicarbonate with a particle size distribution between 400 μm and 1200 μm
	Silicate	Amorphous Sodium Silicate ($\text{SiO}_2\text{:Na}_2\text{O}$; 2.0 ratio)
	Sulfate	Anhydrous sodium sulfate
	PAE	ethoxylated tetraethylene pentamine
10	PIE	ethoxylated polyethylene imine
	PAEC	methyl quaternized ethoxylated dihexylene triamine
	MA/AA	Copolymer of 1:4 maleic/acrylic acid, average molecular weight about 70,000.
	CMC	Sodium carboxymethyl cellulose
15	Protease	Proteolytic enzyme of activity 4KNPU/g sold by NOVO Industries A/S under the tradename Savinase
	Cellulase	Cellulytic enzyme of activity 1000 CEVU/g sold by NOVO Industries A/S under the tradename Carezyme
	Amylase	Amylolytic enzyme of activity 60KNU/g sold by NOVO Industries A/S under the tradename Termamyl 60T
20	Lipase	Lipolytic enzyme of activity 100kLU/g sold by NOVO Industries A/S under the tradename Lipolase
	Percarbonate	Sodium Percarbonate of nominal formula $2\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$
	NaDCC	Sodium dichloroisocyanurate
25	TAED	Tetraacetythylenediamine
	DTPMP	Diethylene triamine penta (methylene phosphonate), marketed by Monsanto under Tradename Dequest 2060
	Photoactivated bleach	Sulfonated Zinc Phthalocyanine bleach encapsulated in dextrin soluble polymer

HEDP	1,1-hydroxyethane diphosphonic acid
SRP 1	Sulfobenzoyl end capped esters with oxyethylene oxy and terephthaloyl backbone
SRP 2	sulfonated ethoxylated terephthalate polymer
5 SRP 3	methyl capped ethoxylated terephthalate polymer
Isofol 16	Condea trademark for C16 (average) Guerbet alcohols
CaCl ₂	Calcium chloride
MgCl ₂	Magnesium chloride
DTPA	Diethylene triamine pentaacetic acid

10

EXAMPLES 10A to 10E: Nonaqueous Liquid Laundry Detergent compositions

Non-limiting examples of bleach-containing nonaqueous liquid laundry detergent are prepared as follows.

Preparation of LAS Powder for Use as a Structurant

15 Sodium C₁₂ linear alkyl benzene sulfonate (NaLAS) is processed into a powder containing two phases. One of these phases is soluble in the non-aqueous liquid detergent compositions herein and the other phase is insoluble. It is the insoluble fraction which serves to add structure and particle suspending capability to the non-aqueous phase of the compositions herein.

20 NaLAS powder is produced by taking a slurry of NaLAS in water (approximately 40-50% active) combined with dissolved sodium sulfate (3-15%) and hydrotrope, sodium sulfosuccinate (1-3%). The hydrotrope and sulfate are used to improve the characteristics of the dry powder. A drum dryer is used to dry the slurry into a flake. When the NaLAS is dried with the sodium sulfate, two distinct phases are created within the flake. The
25 insoluble phase creates a network structure of aggregate small particles (0.4-2 um) which allows the finished non-aqueous detergent product to stably suspend solids.

The NaLAS powder prepared according to this example has the following makeup shown in Table I.

TABLE I

LAS Powder

<u>Component</u>	<u>Wt. %</u>
NaLAS	85%
Sulfate	11%
Sulfosuccinate	2%
Water	2.5%
Unreacted, etc.	balance to 100%
% insoluble LAS	17%
# of phase (via X-ray diffraction)	2

Non-aqueous based heavy duty liquid laundry detergent compositions which comprise the capped nonionic surfactants of the present invention are presented below.

5

Component	A	B	C	D	E
LAS, From Example I	15	15	15	15	5
Nonionic from example 1	21.5	15	-	5	-
Nonionic from example 3	-	-	-	-	25
Nonionic from example 4	-	-	10	5	-
C12,13EO5	-	6.5	11.5	16.5	6.5
BPP	19.5	19	19	19	19
Sodium citrate dihydrate	7	7	7	7	7
Bleach activator	6	6	6	6	6
Sodium carbonate	9	9	9	9	9
Maleic-acrylic copolymer	3	3	3	3	3
Colored speckles	0.4	0.4	0.4	0.4	0.4

EDDS	1	1	1	1	1
Cellulase Prills	0.1	0.1	0.1	0.1	0.1
Amylase Prills	0.4	0.4	0.4	0.4	0.4
Ethoxylated diamine quat	1.3	1.3	1.3	1.3	1.3
Sodium Perborate	12	12	12	12	12
Optionals including: brightener, colorant, perfume, thickener, suds suppressor, colored speckles etc.	balance	balance	balance	balance	balance
	100%	100%	100%	100%	100%

The resulting compositions are stable, anhydrous heavy-duty liquid laundry detergents which provide excellent rates of mixing with water as well as good stain and soil removal performance when used in normal fabric laundering operations.

5

EXAMPLE 11: Hand Dishwashing Liquid compositions

The following examples further illustrate the invention herein with respect to a hand dishwashing liquid.

	<u>Ingredient</u>	<u>% (wt.)</u>	<u>Range (% wt.)</u>
10	Nonionic from example 8	5.0	1 - 20
	MBAE ₂ S ₁₅	2.0	0.5-10
	Ammonium C ₁₂₋₁₃ alkyl sulfate	7.0	2-35
	C ₁₂ -C ₁₄ ethoxy (1) sulfate	20.5	5-35
	Coconut amine oxide	2.6	2-5
15	Betaine/Tetronic 704®**	0.87-0.10	0-2 (mix)
	Alcohol Ethoxylate C ₉₋₁₁ E ₉	1.0	0.5-10
	Ammonium xylene sulfonate	4.0	1-6
	Ethanol	4.0	0-7
	Ammonium citrate	0.06	0-1.0
20	Magnesium chloride	3.3	0-4.0

	Calcium chloride	2.5	0-4.0
	Ammonium sulfate	0.08	0-4.0
	Perfume	0.18	0-0.5
	Maxatase [®] protease	0.50	0-1.0
5	Water and minors	-----Balance-----	

** Cocoalkyl betaine.

EXAMPLES 12 to 16: Shampoo compositions

		<u>Example Number</u>				
<u>Component</u>		<u>12</u>	<u>13</u>	<u>14</u>	<u>15</u>	<u>16</u>
10	Ammonium laureth-2 sulfate	5	3	2	10	8
	Ammonium lauryl sulfate	5	5	4	5	8
	Nonionic from example 3	2	0	0	4	7
	Nonionic from example 6	0	3	0	0	0
	Nonionic from example 7	0	0	4	1	0
15	Cocamide MEA	0	0.68	0.68	0.8	0
	PEG 14M	0.1	0.35	0.5	0.1	0
	Cocoamidopropylbetaine	2.5	2.5	0	0	1.5
	Cetylalcohol	0.42	0.42	0.42	0.5	0.5
	Stearylalcohol	0.18	0.18	0.18	0.2	0.18
20	Ethylene glycol distearate	1.5	1.5	1.5	1.5	1.5
	Dimethicone ¹	1.75	1.75	1.75	1.75	2.0
	Perfume solution	0.45	0.45	0.45	0.45	0.45
	DMDM hydantoin	0.37	0.37	0.37	0.37	0.37
	Color solution (ppm)	64	64	64	64	64
25	Water and minors	----- q. s. to 100% -----				

1. Dimethicone is a 40(gum)/60(fluid) weight ratio blend of SE-76 dimethicone gum available from General Electric Silicones Division and a dimethicone fluid having a viscosity of 350 centistokes.

EXAMPLES 17 to 32: Granular Laundry Detergents

The following laundry detergent compositions are prepared in accord with the invention:

	17	18	19	20	21	22
MBAS _{14.4}	8.0	4.0	4.0	8.0	4.0	4.0
C45AS	-	4.0	2.8	-	4.0	2.8
LAS	-	-	1.2	-	-	1.2
Nonionic from example 4	-	3.4	-	1.7	-	-
Nonionic from example 1	3.4	-	-	1.7	-	3.4
Nonionic from example 2(b)	-	-	3.4	-	3.4	-
AQA	0.4	0.5	0.6	0.8	0.8	0.8
Zeolite A	18.1	18.1	18.1	18.1	18.1	18.1
Carbonate	13.0	13.0	13.0	27.0	27.0	27.0
Silicate	1.4	1.4	1.4	3.0	3.0	3.0
Sulfate	26.1	26.1	26.1	26.1	26.1	26.1
PB4	9.0	9.0	9.0	9.0	9.0	9.0
TAED	1.5	1.5	1.5	1.5	1.5	1.5
DTPMP	0.25	0.25	0.25	0.25	0.25	0.25
HEDP	0.3	0.3	0.3	0.3	0.3	0.3
Protease	0.26	0.26	0.26	0.26	0.26	0.26
Amylase	0.1	0.1	0.1	0.1	0.1	0.1
MA/AA	0.3	0.3	0.3	0.3	0.3	0.3
CMC	0.2	0.2	0.2	0.2	0.2	0.2
Photoactivated bleach	15 ppm	15 ppm	15 ppm	15 ppm	15 ppm	15 ppm
Brightener 1	0.09	0.09	0.09	0.09	0.09	0.09
Perfume	0.3	0.3	0.3	0.3	0.3	0.3
Silicone antifoam	0.5	0.5	0.5	0.5	0.5	0.5
Misc/minors to 100%						

Density in g/litre	850	850	850	850	850	850
--------------------	-----	-----	-----	-----	-----	-----

The following laundry detergent compositions are prepared in accord with the invention:

	23	24	25	26	27
MBAS14.4	22	16.5	11	1 - 5.5	10 - 25
Any Combination of: C45 AS C45E1S LAS C16 SAS C14-17 NaPS C14-18 MES MBAE2S14.3	0	1 - 5.5	11	16.5	0 - 5
AQA	2	2	2	2	0.5 - 4
Nonionic from example 2g	-	1.5	-	-	1 - 4
Nonionic from example 5	1.5	-	-	1.5	1 - 4
Nonionic from example 1	-	-	1.5	-	1 - 4
Zeolite A	27.8	27.8	27.8	27.8	20 - 30
PAA	2.3	2.3	2.3	2.3	0 - 5
Carbonate	27.3	27.3	27.3	27.3	20 - 30
Silicate	0.6	0.6	0.6	0.6	0 - 2
PB1	1.0	1.0	1.0	1.0	0 - 3
Protease	0 - 0.5	0 - 0.5	0 - 0.5	0 - 0.5	0 - 0.5
Cellulase	0 - 0.3	0 - 0.3	0 - 0.3	0 - 0.3	0 - 0.5
Amylase	0 - 0.5	0 - 0.5	0 - 0.5	0 - 0.5	0 - 1

SRP 1	0.4	0.4	0.4	0.4	0 - 1
Brightener 1 or 2	0.2	0.2	0.2	0.2	0 - 0.3
PEG	1.6	1.6	1.6	1.6	0 - 2
Sulfate	5.5	5.5	5.5	5.5	0 - 6
Silicone Antifoam	0.42	0.42	0.42	0.42	0 - 0.5
Moisture & Minors	---Balance---				
Density (g/L)	663	663	663	663	600 - 700

The following laundry detergent compositions are prepared in accord with the invention:

	28	29	30	31	32
MBAS14.4	16.5	12.5	8.5	4	1 - 25
Any Combination of: C45 AS C45E1S LAS C16 SAS C14-17 NaPS C14-18 MES MBAE2S14.3	0 - 6	10	14	18.5	0 - 20
AQA	2	2	2	2	1 - 4
TFAA	1.6	1.6	1.6	1.6	0 - 4
Nonionic from example 6	5	-	-	5	1 - 6
Nonionic from example 4	-	5	-	-	1 - 6
Nonionic from example 3	-	-	5	-	1 - 6
Zeolite A	15	15	15	15	10 - 30
NaSKS-6	11	11	11	11	5 - 15
Citrate	3	3	3	3	0 - 8
MA/AA	4.8	4.8	4.8	4.8	0 - 8

HEDP	0.5	0.5	0.5	0.5	0 - 1
Carbonate	8.5	8.5	8.5	8.5	0 - 15
Percarbonate or PB1	20.7	20.7	20.7	20.7	0 - 25
TAED	4.8	4.8	4.8	4.8	0 - 8
Protease	0.9	0.9	0.9	0.9	0 - 1
Lipase	0.15	0.15	0.15	0.15	0 - 0.3
Cellulase	0.26	0.26	0.26	0.26	0 - 0.5
Amylase	0.36	0.36	0.36	0.36	0 - 0.5
SRP 1	0.2	0.2	0.2	0.2	0 - 0.5
Brightener 1 or 2	0.2	0.2	0.2	0.2	0 - 0.4
Sulfate	2.3	2.3	2.3	2.3	0 - 25
Silicone Antifoam		0.4	0.4	0.4	0 - 1
Moisture & Minors	---Balance---				
Density (g/L)	850	850		850	850

EXAMPLES 33 to 40: Hard Surface Cleaners

Mixing the listed ingredients in the listed proportions made the following compositions.

These compositions were used neat to clean marble and dilute to clean lacquered wooden

5 floors. Excellent cleaning and surface safety performance was observed.

	33	34	35	36	37	38	39	40
Nonionic from example 8	3.0	-	1.0	-	3.2	-	-	-
Nonionic from example 1	-	3.0	2.0	-	-	-	4.0	8.0
Nonionic from example 3	-	-	2.0	3.2	-	3.2	4.0	-
C23E3	1.0	1.0	1.5	1.3	1.3	1.5	3.0	3.5
C24E21	2.0	2.0	2.5	1.9	1.9	2.0	5.0	6.0
NaPS	2.0	1.5	1.2	1.2	1.0	1.7	3.0	2.5
NaTS	1.2	3.0	2.2	2.0	2.0	1.5	4.0	5.0
MgSO4	0.20	0.9	0.30	0.50	1.3	2.0	1.0	3.0
Citrate	0.3	1.0	0.5	0.75	1.8	3.0	1.5	6.0

NaHCO ₃	0.06	0.1	-	0.1	-	0.2	-	-
Na ₂ HPO ₄	-	-	0.1	-	0.3	-	-	-
Na ₂ H ₂ P ₂ O ₇	-	-	-	-	-	-	0.2	0.5
pH	8.0	7.5	7.0	7.25	8.0	7.4	7.5	7.2
Water and Minors	q.s. to 100%							

EXAMPLE 41

Automatic dishwashing compositions:

Ingredients:Weight %

	<u>A</u>	<u>B</u>
Sodium Tripolyphosphate (STPP)	24.0	45.0
Sodium Carbonate	20.0	13.5
Hydrated 2.0r Silicate	15.0	13.5
Nonionic Surfactant ¹	3.0	3.0
C ₁₄ Amine Oxide	1.0	1.0
Polymer ²	4.0	--
Protease (4% active)	0.83	0.83
Amylase (0.8% active)	0.5	0.5
Perborate Monohydrate (15.5% active AvO) ³	14.5	14.5
Cobalt Catalyst ⁴	0.008	--
Dibenzoyl Peroxide (18% active)	4.4	4.4
Water, Sodium Sulfate, Misc.	Balance	Balance

5

¹ Nonionic surfactant according to Example 1.² Terpolymer selected from either 60% acrylic acid/20% maleic acid/20% ethyl acrylate, or 70% acrylic acid/10% maleic acid/20% ethyl acrylate.³ The AvO level of the above formula is 2.2%.

⁴ Pentaamineacetatocobalt(III) nitrate prepared as described hereinbefore; may be replaced by MnTacN.

The following examples further illustrate phosphate built ADD compositions which contain a bleach/enzyme particle, but are not intended to be limiting thereof. These compositions are suitable for use in the methods of the present invention. All percentages noted are by weight of the finished compositions, other than the perborate (monohydrate) component, which is listed as AvO.

EXAMPLES 42-43

<u>Ingredients:</u>	<u>Weight %</u>	
	<u>42</u>	<u>43</u>
STPP	30.0	32.0
Na ₂ CO ₃	30.5	20.5
2 R Silicate (SiO ₂)	8.0	4.0
Catalyst ¹	0.008	0.004
Savinase TM 12T	--	1.1
Protease D	0.9	--
Perborate (AvO)	5.0	0.7
Polymer ²	4.0	--
Dibenzoyl Peroxide	0.2	0.15
Paraffin	0.5	0.5
Benzotriazole	0.10	0.3
C ₁₄ Amine Oxide	0.5	0.5
Nonionic Surfactant ³	2.0	2.0
Sodium Sulfate, Moisture	----- Balance -----	

10 ¹ Pentaamineacetatocobalt(III) nitrate; may be replaced by MnTacN.

² Polyacrylate or Acusol 480N or polyacrylate/polymethacrylate copolymers.

³ Nonionic surfactant according to Example 7.

In compositions of Examples 42 and 43, respectively, the catalyst and enzymes are introduced into the compositions as 200-2400 micron composite particles that are prepared by spray coating, fluidized bed granulation, marummarizing, prilling, or flaking/grinding operations. If desired, the protease and amylase enzymes may be separately formed into their respective catalyst/enzyme composite particles, for reasons of stability, and these separate compositions added to the compositions.

The following examples further illustrate ADD granular compositions with chlorine bleach suitable for use in the methods of this present invention.

EXAMPLE 44-45

<u>Ingredients:</u>	<u>Weight %</u>	
	<u>44</u>	<u>45</u>
STPP	25	31
Na ₂ CO ₃	23.0	15.0
2 R Silicate (SiO ₂)	17.5	25.0
Hypochlorite	1.0	3.0
Polymer ¹	2.0	--
Dibenzoyl Peroxide	--	0.15
Paraffin	1.0	1.0
C ₁₆ Amine Oxide	0.5	1.0
Nonionic Surfactant ²	2.0	3.0
Sodium Sulfate, Moisture	----- Balance -----	

¹ Polyacrylate or Acusol 480N or polyacrylate/polymethacrylate copolymers

³ Nonionic surfactant according to Example 8.

The following examples further illustrate ADD liquid-gel compositions suitable for use in the methods of this present invention.

EXAMPLES 46-47

<u>Ingredients:</u>	<u>Weight %</u>	
	<u>46</u>	<u>47</u>

STPP	32.0	25.0
Na ₂ CO ₃	0.7	2.0
2 R Silicate (SiO ₂)	0.3	1.0
Savinase™ 12T	2.0	1.0
Termamyl™	1.4	0.5
Perborate (AvO)	3.5	--
C ₁₄ Amine Oxide	0.8	0.8
Nonionic Surfactant ¹	3.5	3.5
Sodium Sulfate, Moisture	----- Balance -----	

¹ Nonionic surfactant according to Example 3.

The following examples further illustrate ADD rinse aid compositions suitable for use in the methods of this present invention.

EXAMPLES 48-49

5	<u>Ingredients:</u>	<u>Weight %</u>	
		<u>48</u>	<u>49</u>
	Citric Acid	10.0	15.0
	Ethanol	5.0	10.0
	HEDP Acid ¹	1.0	0.7
	Sodium Cumene Sulfonate	15.0	10.0
	Polymer ²	--	1.0
	C ₁₄ Amine Oxide	2.0	0.5
	Nonionic Surfactant ³	8.0	8.0
	Nonionic Surfactant ⁴	6.0	-
	Moisture	----- Balance -----	

¹ 1-Hydroxyethylidene-1,1-diphosphonic acid

² Polyacrylate or Acusol 480N or polyacrylate/polymethacrylate copolymers

³ Nonionic surfactant according to Example 1.

⁴ Nonionic surfactant according to Example 5.

The following examples further illustrate ADD tablet compositions suitable for use in the methods of this present invention.

EXAMPLES 54-55

5 <u>Ingredients:</u>	<u>50</u>	<u>Weight %</u>	<u>51</u>
STPP	48.0		30
Na ₂ CO ₃	15.0		25.0
2 R Silicate (SiO ₂)	4.0		8.0
Catalyst ¹	0.008		0.004
Savinase TM 12T	--		1.0
Termamyl TM	0.6		0.5
Perborate (AvO)	10.0		15.0
Polymer ²	2.0		2.0
Dibenzoyl Peroxide	0.2		0.15
Paraffin	1.0		1.0
Benzotriazole	0.5		0.5
C ₁₄ Amine Oxide	1.0		1.0
Nonionic Surfactant ³	3.0		3.0
Sodium Sulfate, Moisture	----- Balance -----		

¹ Pentaamineacetatocobalt(III) nitrate; may be replaced by MnTacN

² Polyacrylate or Acusol 480N or polyacrylate/polymethacrylate copolymers

³ Nonionic surfactant according to Example 2f.